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Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,

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THE PERIODIC TABLE.*

PERIODS.	GROUP O.	GROUP I	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period .	2 He 4.002	1 H 1.0078 3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.00	7 N 14.008 15 P 31.02	8 O 16.000	9 F 19.00	26 Fe 55.84 27 Co 58.94 28 Ni 58.69
Second short period .	10 Ne 20.183	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 S 32.06	16 Cl 35.457	17 Br 79.916	29 Cu 63.57
First long period { Even series Odd "	18 Ar 39.944	19 K 39.096 20 Ca 40.08	21 Sc 44.96 22 Ti 47.90 23 V 50.95 24 Cr 52.01 25 Mn 54.93	26 Fe 55.84 27 Co 58.94 28 Ni 58.69	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	44 Ru 101.7 45 Rh 102.91 46 Pd 106.7
Second long period { Even series Odd "	36 Kr 83.7	37 Rb 85.44 38 Sr 87.63	39 Y 88.92 40 Zr 91.22 41 Nb 92.91 42 Mo 95.94 43 Tc 98.91 44 Ru 101.7 45 Rh 102.91 46 Pd 106.7	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	47 Ag 107.88
Third long period .	54 Xe 131.3	55 Cs 132.91	56 Ba 137.36	57 La 138.92	58 Ce 140.12 59 Pr 140.92 60 Nd 144.27 61 Pm 144.91 62 Sm 150.43 63 Eu 151.96 64 Gd 157.25 65 Tb 158.93 66 Dy 162.50 67 Ho 164.93 68 Er 167.27 69 Tm 168.93 70 Yb 173.05 71 Lu 175.07	72 Hf 178.49 73 Ta 180.94 74 W 183.85 75 Re 186.21 76 Os 191.5 77 Ir 192.22 78 Pt 195.08 79 Au 196.97 80 Hg 200.59 81 Tl 204.38 82 Pb 207.2 83 Bi 208.98 84 Po [210] 85 At [210] 86 Rn 222	86 Rn 222	87 Fr 223 88 Ra 226.075 89 Ac 227.033 90 Th 232.038 91 Pa 231.036 92 U 238.029 93 Np 237.048 94 Pu 244.064 95 Am 243.061 96 Cm 247.070 97 Bk 247.070 98 Cf 251.080 99 Es 252.083 100 Fm 257.103	101 La 138.905 102 Ce 140.116 103 Pr 140.908 104 Nd 144.242 105 Pm 144.913 106 Sm 150.36 107 Eu 151.964 108 Gd 157.254 109 Tb 158.925 110 Dy 162.500 111 Ho 164.930 112 Er 167.259 113 Tm 168.930 114 Yb 173.054 115 Lu 175.077 116 Hf 178.49 117 Ta 180.948 118 W 183.848 119 Re 186.207 120 Os 191.224 121 Ir 192.222 122 Pt 195.084 123 Au 196.967 124 Hg 200.596 125 Tl 204.384 126 Pb 207.2 127 Bi 208.980 128 Po [210] 129 At [210] 130 Rn 222

* The Revised International Atomic Weights for 1936 are adopted in this Table.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY
J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
CARNEGIE GOLD MEDALLIST.

VOLUME VI., PART V.
ANTIMONY AND BISMUTH.

BY
W. E. THORNEYCROFT, B.Sc.

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GENERAL INTRODUCTION TO THE SERIES.

DURING the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches : namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned ; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the original scheme, in addition to a detailed account of the elements of Group O, the general principles of Inorganic and Physical Chemistry were discussed in Volume I. It was later felt, however, that this arrangement was hardly satisfactory, and an Introduction to these principles is now afforded by my Text-book of Physical Chemistry, Volumes I. and II. (1932-35), whilst in future editions Volume I. of this Series will deal with the Inert Gases alone.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX.

under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferrocyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:—

Hydrogen =	1.00762.	Oxygen =	16.000.
Sodium =	22.996.	Sulphur =	32.065.
Potassium =	39.100.	Fluorine =	19.015.
Silver =	107.880.	Chlorine =	35.457.
Carbon =	12.003.	Bromine =	79.916.
Nitrogen =	14.008.	Iodine =	126.920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and, moreover, it renders the data for the different elements strictly comparable throughout the whole series.

Since the original scheme was drawn up in 1912, enormous progress has been made in all branches of chemistry, and the original intention of devoting one book only to each Vertical Group in the Periodic Table has had to be abandoned. In several cases it has been necessary to devote a whole book to a single element, as, for example, in the cases of oxygen, nitrogen, phosphorus and arsenic. Further, a separate volume has been devoted to the Metal-Ammines and a comprehensive account of the Organometallic Derivatives is given in Volume XI., which is being issued in four parts.

The Editor would draw attention to the unsatisfactory state of the nomenclature of organometallic compounds in general. The designations of compounds in Volume XI. are those used in the original memoirs, since any attempt to alter these in a work of that description would only complicate matters.

Our aim has not been to make the volumes absolutely exhaustive,

as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii-xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi-xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the Authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

September 1936.

PREFACE.

ACCORDING to the Oxford English Dictionary, the origin of both names *antimony* and *bismuth* is unknown, and, unfortunately, something of this obscurity appears to overshadow many of the problems connected with the chemistry of these two elements and their compounds. It is possible that this arises from their position as the last two elements of Sub-group B of Group V. of the Periodic Classification. In accordance with that position, although they retain many of the characteristics of the group as a whole (which have been considered in Part I. of this Volume), they possess in addition definite basigenic properties. Thus, many of their compounds readily undergo hydrolysis, but frequently the hydrolysis is not complete, intermediate products of great complexity being produced, the natures of which have not yet been fully established. Moreover, there is evidence to show that the process of hydrolysis is not always continuous, but is complicated by secondary reactions between the hydrolytic products and the solutions from which they are formed. These factors have rendered it extremely difficult to obtain compounds of these two elements in a state of purity, the perplexities arising from this being exemplified in the controversies concerning the atomic weights of the two elements, which have been concluded satisfactorily only within the last twenty years.

Another feature of these two elements is the tendency of both to form complexes. In some cases these complexes have been shown to partake of the nature of anions; in others, their true nature is not fully known. The study of these questions involves the conception of valency, but, in this book, it has been deemed advisable to discuss the compounds of the two elements in the light of the older valency theories, in which these elements were regarded as existing in one of the two states ter- or quinque-valent. Further study of antimony and bismuth in combination should throw considerable light on valency relationships and should prove of great value not merely in elucidating the chemistry of the two elements themselves, but in advancing the knowledge of structural chemistry in general.

In the metallic state antimony and bismuth are not very widely employed in industry or the arts, although the former element is an essential component of some exceedingly important alloys, such as type metal and bearing metal, the many varieties of which play such a conspicuous part in modern civilisation. Bismuth is chiefly valuable as a component of fusible alloys; this is perhaps due not so much to its own low melting point as to its great tendency to form eutectics. It is noteworthy that bismuth does not enter largely into combination, nor into solid solution, with other metals.

The anisotropic nature of the crystals of these two metals has attracted considerable attention from physicists; with the development of the technique for the production of single crystals the examination

of the physical properties of bismuth in particular has been very extensive. Many of the published results, however, must be accepted with reserve, as the investigators did not appear to appreciate fully that the physical condition of the material employed was of as much importance as the chemical purity. The close alliance which has arisen in recent years between physicists and metallurgists cannot fail to bear fruit in this field of research; and it is possible that a careful examination of the physical properties of the two elements antimony and bismuth may throw considerable light on the nature of the metallic state, in spite of the fact that they themselves are such imperfect metals.

An attempt has been made in this book to describe the state of knowledge of the chemistry of the two elements and their compounds up to the end of 1934. Many themes of a physico-chemical nature have received but a mere mention; it is hoped, however, that references to original sources will enable the reader to follow up those themes with a minimum of labour.

In addition to the literature cited, much assistance has been obtained from Gmelin-Kraut, "*Handbuch der anorganischen Chemie*," and from "*A Comprehensive Inorganic Chemistry*," by J. W. Mellor.

Finally, the author very gratefully acknowledges his indebtedness to Messrs. Cooke, Troughton and Simms, Ltd., of York, for permission to reproduce the Plate showing the macrostructure of antimony (from a photograph by Mr. M. C. Oldham of the English Steel Corporation); to Dr. E. B. R. Prideaux and Mr. R. H. Vallance for their valuable assistance in proof-reading; and to the General Editor of the Series, Dr. J. Newton Friend, not only for the sympathy and courtesy with which he has smoothed over many difficulties during the preparation of this book, but also for his active co-operation in certain sections, notably in those on the atomic weights.

W. E. THORNEYCROFT.

WOLLASTON, STOURBRIDGE.

September 1936.

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LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Afhandl. Fys. Kem.</i> . . .	Afhandlingar i Fysik, Kemi och Mineralogi.
<i>Amer. Chem. J.</i> . . .	American Chemical Journal.
<i>Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . .	The Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim.</i> . . .	Annales de Chimie (1719-1815, and 1914+).
<i>Ann. Chim. anal.</i> . . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
<i>Ann. Chim. Phys.</i> . . .	Annales de Chimie et de Physique (Paris) (1816-1913).
<i>Ann. Mines</i> . . .	Annales des Mines.
<i>Ann. Pharm.</i> . . .	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i> . . .	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i> . . .	Annalen der Physik (1799-1818, and 1900+).
<i>Ann. Physik, Beibl.</i> . . .	Annalen der Physik, Beiblattes.
<i>Ann. Sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.
<i>Arbeiten Kaiserl. Gesundheits- amte</i> . . .	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmac.</i> . . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i> . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physique et naturelles, Genève.
<i>Atti Acc. Torino</i> . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia Lincei.
<i>B.A. Reports</i> . . .	British Association Reports.
<i>Ber.</i> . . .	Berichte der deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i> . . .	See <i>Sitzungsber. K. Akad. Wiss. Berlin</i> .
<i>Ber. deut. pharm. Ges.</i> . . .	Berichte der deutschen pharmazeutischen Gesellschaft.
<i>Ber. deut. physikal. Ges.</i> . . .	Berichte der deutschen physikalischen Gesellschaft.
<i>Bot. Zeit.</i> . . .	Botanische Zeitung.
<i>Bul. Soc. Stiințe Cluj.</i> . . .	Buletinul Societății de Stiințe din Cluj.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i> . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. de Belg.</i> . . .	Bulletin de la Société chimique Belgique.
<i>Bull. Sci. Pharmacol.</i> . . .	Bulletin des Sciences Pharmacologiques.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. franç. Min.</i> . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i> . . .	Bulletin de la Société minéralogique de France.
<i>Bull. U.S. Geol. Survey</i> . . .	Bulletins of the United States Geological Survey.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie.
<i>Chem. Ind.</i> . . .	Die Chemische Industrie.
<i>Chem. News</i> . . .	Chemical News.
<i>Chem. Weekblad</i> . . .	Chemisch Weekblad.
<i>Chem. Zeit.</i> . . .	Chemiker Zeitung (Östhen).
<i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.
<i>Compt. rend.</i> . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
<i>Crell's Annalen</i> . . .	Chemische Annalen für die Freunde der Naturlehre, von L. Crell.
<i>Dingl. poly. J.</i> . . .	Dingler's polytechnisches Journal.

ABBREVIATED TITLE.	JOURNAL.
<i>Drude's Annalen</i> . . .	Annalen der Physik (1900-1906).
<i>Electroch. Met. Ind.</i> . . .	Electrochemical and Metallurgical Industry.
<i>Eng. and Min. J.</i> . . .	Engineering and Mining Journal.
<i>Gazzetta</i> . . .	Gazzetta chimica italiana.
<i>Gehlen's allg. J. Chem.</i> . . .	Allgemeines Journal der Chemie.
<i>Geol. Mag.</i> . . .	Geological Magazine.
<i>Gilbert's Annalen</i> . . .	Annalen der Physik (1799-1824).
<i>Giorn. di Scienze Naturali ed Econ.</i> . . .	Giornale di Scienze Naturali ed Economiche.
<i>Helv. Chim. Acta</i> . . .	Helvetica Chim. Acta.
<i>Int. Zeitsch. Metallographie</i> . . .	Internationale Zeitschrift für Metallographie.
<i>Jahrb. k. k. geol. Reichsanst.</i> . . .	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
<i>Jahrb. Miner.</i> . . .	Jahrbuch für Mineralogie.
<i>Jahresber.</i> . . .	Jahresbericht über die Fortschritte der Chemie.
<i>Jenaische Zeitsch.</i> . . .	Jenaische Zeitschrift für Naturwissenschaft.
<i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Chem. Soc.</i> . . .	Journal of the Chemical Society.
<i>J. Chim. phys.</i> . . .	Journal de Chimie physique.
<i>J. Gasbeleuchtung</i> . . .	Journal für Gasbeleuchtung.
<i>J. Geology</i> . . .	Journal of Geology.
<i>J. Ind. Eng. Chem.</i> . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Metals</i> . . .	Journal of the Institute of Metals.
<i>J. Miner. Soc.</i> . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>J. Pharm. Chim.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physique</i> . . .	Journal de Physique.
<i>J. prakt. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia (Petrograd).
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>Landw. Jahrb.</i> . . .	Landwirtschaftliche Jahrbücher.
<i>Mem. Coll. Sci. Kyōtō.</i> . . .	Memoirs of the College of Science, Kyōtō Imperial University.
<i>Mém. Paris Acad.</i> . . .	Mémoires présentés par divers savants à l'Académie de Sciences de l'Institut de France.
<i>Monatsh.</i> . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. scient.</i> . . .	Moniteur scientifique.
<i>Münch. Med. Wochenschr.</i> . . .	Münchener Medizinische Wochenschrift.
<i>Nature</i> . . .	Nature.
<i>Nuovo Cim.</i> . . .	Il nuovo Cimento.
<i>Oesterr. Chem. Zeit.</i> . . .	Oesterreichische Chemiker-Zeitung.
<i>Öfvers. K. Vet.-Akad. Förh.</i> . . .	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
<i>Pflüger's Archiv</i> . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Post</i> . . .	Pharmazeutische Post.
<i>Pharm. Zentr.-h.</i> . . .	Pharmazeutische Zentralhalle.
<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh, and Dublin).
<i>Phil. Trans.</i> . . .	Philosophical Transactions of the Royal Society of London.
<i>Phys. Review</i> . . .	Physical Review.
<i>Physikal. Zeitsch.</i> . . .	Physikalische Zeitschrift.
<i>Pogg. Annalen</i> . . .	Poggendorff's Annalen der Physik und Chemie (1824-1877).
<i>Proc. Chem. Soc.</i> . . .	Proceedings of the Chemical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i> . . .	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
<i>Proc. Roy. Irish Acad.</i> . . .	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Phil. Soc. Glasgow</i> . . .	Proceedings of the Royal Philosophical Society of Glasgow.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society of London.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.

ABBREVIATED TITLE.	JOURNAL.
<i>Rec. Trav. chim.</i> . . .	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
<i>Roy. Inst. Reports</i> . . .	Reports of the Royal Institution.
<i>Schweigger's J.</i> . . .	Journal für Chemie und Physik.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . .	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i> . . .	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
<i>Techn. Jahresber.</i> . . .	Jahresbericht über die Leistungen der Chemischen Technologie.
<i>Trans. Amer. Electrochem. Soc.</i> . . .	Transactions of the American Electrochemical Society.
<i>Trans. Chem. Soc.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Inst. Min. Eng.</i> . . .	Transactions of the Institution of Mining Engineers.
<i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i> . . .	Travaux et Mémoires du Bureau International des Poids et Mesures.
<i>Verh. Ges. deut. Naturforsch. Aerzte.</i> . . .	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Wied. Annalen</i> . . .	Wiedemann's Annalen der Physik und Chemie (1877-1899).
<i>Wissenschaftl. Abhandl. phys.-tech. Reichsanst.</i> . . .	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem.</i> . . .	Kritische Zeitschrift für Chemie.
<i>Zeitsch. Chem. Ind. Kolloide</i> . . .	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
<i>Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Kristallographie und Mineralogie.
<i>Zeitsch. Nahr. Genuss-m.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Photochem.</i> . . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

FOR the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32-35	4-6	...	5-8	90	...
1	...	36-39	7-9	...	8-11	91	...
2	...	40-43	10-12	...	11-14	92	...
3	...	44-47	13-15	...	14-17	93	...
4	..	48-51	16-18	...	17-20	94	...
1805	...	52-55	19-21	...	20-23	95	...
6	...	56-60	22-24	...	23-26	96	...
7	...	61-64	25-27	...	26-29	97	...
8	...	65-68	28-30	...	29-32	98	...
9	...	69-72	31-33	(1) 1*	33, 34	99	...
1810	...	73-76	34-36	2	35, 36	100	...
11	...	77-80	37-39	3	37, 38	101	...
12	...	81-84	40-42	4	39, 40	102	...
13	...	85-88	43-45	5	41, 42	103	...
14	...	89-92	46-48	6	43, 44	104	...
1815	...	93-96	49-51	(2) 1	45, 46	105	...
16	...	(2) 1-3	52-54	2	47, 48	106	...
17	..	4-6	1, 2	55-57	3	49, 50	107	...
18	...	7-9	3	58-60	4	51, 52	108	...
19	(1) 1	10-12	4	61-63	5	53, 54	109	...
1820	2	13-15	5	...	1-3	64-66	6	55, 56	110	...
21	3	16-18	6	...	4-6	67-69	7	57, 58	111	...
22	4, 5	19-21	7	1, 2	7-9	70-72	8	59, 60	112	...
23	6	22-24	8	3-6	10-12	73-75	9	61, 62	113	...
24	7, 8	25-27	9	7-10	13-15	76	10	63, 64	114	1, 2
1825	9	28-30	10, 11	11-14	16-18	Continued as Pogg. Annalen.	11	65, 66	115	3-5
26	10, 11	31-33	12, 13	15-19	19-22		12	67, 68	116	6-8
27	12	34-36	(2) 1, 2	20-23	23-26		13	(2) 1, 2	117	9-11
28	13, 14	37-39	3, 4	24-26	27-30		14	3, 4	118	12-14
29	15, 16	40-42	5, 6	27-30	31-34		15	5, 6	119	15-17

* First series known as *Bulletin de Pharmacie*.

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon. scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	43-45	7-8	31-34	35-38	16	7, 8	120	18-20
31	19, 20	...	46-48	...	35-39	39-42	17	9, 10	121	21-23
32	21, 22	...	49-51	(3) 1, 2	40-43	43-47	18	11 (3) 1	122	24-26	1
33	23, 24	5-8	52-55	3, 4	44-47	48-50	19	2, 3	123	27-30	2
34	25-27	9-12	56-57	5, 6	48-50	51-54	20	1-3	...	4, 5	124	31-33
1835	28, 29	13-16	58-60	7, 8	(2) 1-4	...	1	55-58	21	4-6	...	6, 7	125	34-36
36	30, 31	17-20	61-63	9, 10	5-8	...	2, 3	59-62	22	7-9	...	8, 9	126	37-39
37	32, 33	21-24	64-66	11, 12	9-12	...	4, 5	63-66	23	10-12	...	10, 11	127	40-42	3
38	34, 35	25-28	67-69	13, 14	13-16	...	6, 7	67-70	24	13-15	...	12, 13	128	43-45
39	36, 37	29-32	70-72	15, 16	17-20	...	8, 9	71-74	25	16-18	...	14, 15	129	46-48
1840	38, 39	33-36	73-75	17, 18	21-24	...	10, 11	75-78	26	19-21	...	16, 17	130	49-51
41	40, 41	37-40	(3) 1-3	19, 20	25-28	...	12, 13	79-82	27	22-24	...	18, 19	131	52-54
42	42, 43	41-44	4-6	(4) 1, 2	29-32	...	14, 15	83-86	(3) 1, 2	25-27	...	20, 21	132	55-57
43	44, 45	45-48	7-9	3, 4	33-36	...	16, 17	87-90	3, 4	28-30	...	22, 23	133	58-60	4
44	46, 47	49-52	10-12	5, 6	37-40	...	18, 19	91-94	5, 6	31-33	...	24, 25	134	61-63
1845	48-50	53-56	13-15	7, 8	41-44	...	20, 21	95-98	7, 8	34-36	...	26, 27	135	64-66
(2) 1, 2	57-60	57-60	16-18	9, 10	45-48	...	22, 23	99-102	9, 10	37-39	...	28, 29	136	67-69
47	5, 4	61-64	19-21	11, 12	49-52	...	24, 25	103-106	11, 12	40-42	...	30, 31	137	70-72	...	1	...
48	5, 6	65-68	22-24	13, 14	53-56	...	26, 27	107-110	13, 14	43-45	...	32, 33	138	73-75	...	1, 2	...
49	7, 8	69-72	25-27	15, 16	57-60	...	28, 29	111-114	15, 16	46-48	...	34, 35	139	76-78	...	2, 3	...
1850	9, 10	73-76	28-30	17, 18	61-64	...	30, 31	115-118	17, 18	49-51	...	36, 37	140	79-81	...	3	4, 5
51	11, 12	77-80	31-33	20	65-68	...	32, 33	119-122	19, 20	52-54	...	(4) 1, 2	141	82-84	5	4	6, 7
52	13, 14	81-84	34-36	(5) 1, 2	69-72	...	34, 35	123-126	21, 22	55-57	...	3, 4	142	85-87	...	5	8, 9
53	15, 16	85-88	37-39	3, 4	73-76	...	36, 37	127-130	23, 24	58-60	...	5, 6	143	88-90	...	6	10, 11
54	17, 18	89-92	40-42	5, 6	77-80	...	38, 39	131-134	25, 26	61-63	...	7, 8	144	91-93	6, 7	7	12-14
1855	19, 20	93-96	43-45	7, 8	81-84	...	40, 41	135-138	27, 28	64-66	...	9, 10	145	94-96	7	8	15-18
56	21, 22	97-100	46-48	9, 10	85-88	...	42, 43	139-142	29, 30	67-69	...	11, 12	146	97-99	8	9	19-22
57	23, 24	101-104	49-51	11, 12	89-92	...	44, 45	143-146	31, 32	70-72	...	13, 14	147	100-102	9	10	23-27
58	25, 26	105-108	52-54	13, 14	93-96	1	46, 47	147-150	33, 34	73-75	(1) 1	15, 16	148	103-105	...	11	28-33
59	27, 28	109-112	55-57	15, 16	97-100	1	48, 49	151-154	35, 36	76-78	3	17, 18	149	106-108	9, 10	12	34-38

* Often referred to by Series : Series 3, vols. 1-16, 1871-1886 ; Series 4, vols. 1-24, 1887-1910 ; Series 5, vols. 1-9, 1911-1919 (one vol. yearly).

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Pull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Zeit.
1860	...	29, 80	...	113-116	...	58-60	17, 18	101-104	...	2	1, 2
61	...	31, 82	...	117-120	1	61-63	19, 20	105-108	...	3	3, 4
62	...	33, 84	...	121-124	2	64-66	(6) 1, 2	109-112	...	4	5, 6
63	...	35, 86	...	125-128	2	67-69	3, 4	113-116	...	5	7, 8
64	...	37, 88	...	129-132	3	(4) 1-3	5, 6	117-120	...	(2) 1, 2	9, 10
1865	...	39, 40	...	133-136	3, 4	4-6	7, 8	121-124	...	3, 4	11, 12
66	...	41, 42	...	137-140	4	7-9	9, 10	125-128	...	5, 6	13, 14
67	...	43, 44	...	141-144	5	10-12	11, 12	129-132	...	6, 7	15, 16
68	...	45, 46	...	145-148	6	13-15	13, 14	133-136	...	8	17, 18
69	...	47, 48	...	149-152	...	16-18	15, 16	137-140	...	9, 10	19, 20
1870	...	49, 50	...	153-156	7	19-21	17, 18	141-144	...	11, 12	21, 22
71	...	(3) 1, 2	...	157-160	...	22-24	19, 20	145-148	...	13, 14	23, 24
72	...	3, 4	...	161-164	8	25-27	(7) 1, 2	149-160, 201*	...	15, 16	25, 26
73	...	5, 6	...	165-170	...	28-30	3, 4	201-203	...	17, 18	27, 28
74	...	7, 8	...	171-174	...	(6) 1-3	5, 6	204, 205	...	19, 20	29, 30
1875	...	9, 10	...	175-179	...	4-6	7, 8	206, 207	...	21, 22	31, 32
76	...	11, 12	...	180-183	...	7-9	9, 10	208, 209	...	23, 24	33, 34
77	...	13, 14	...	184-189	...	10-12	11, 12	210, 211	...	25, 26	35, 36
78	...	15, 16	...	190-194	...	13-15	13, 14	212, 213	...	27, 28	37, 38
79	...	17, 18	...	195-199	...	16-18	15, 16	214, 215	...	29, 30	39, 40
1880	1, 2	19, 20	...	200-205	...	19-21	17, 18	216, 217	...	31, 32	41, 42
81	2, 3	21, 22	5	206-210	...	22-24	19, 20	218, 219	...	33, 34	43, 44
82	3, 4	23, 24	6	211-215	...	25-27	(8) 1, 2	220	...	35, 36	45, 46
83	4, 5	25, 26	8	216-221	...	28-30	3, 4	221	...	37, 38	47, 48
84	5, 6	27, 28	9	222-226	...	(6) 1-3	5, 6	222	...	39, 40	49, 50
1885	6, 7	29, 30	...	227-231	...	4-6	7, 8	223	...	41, 42	51, 52
86	7, 8	31, 32	10	232-236	...	7-9	9, 10	224	...	43, 44	53, 54
87	9	33, 34	11	237-242	...	10-12	11, 12	225	...	45, 46	55, 56
88	10	35, 36	12	243-249	...	13-15	13, 14	226	...	47, 48	57, 58
89	11	37, 38	13	250-255	...	16-18	15, 16	227	...	49, 50	59, 60
			14		(3) 1, 2	

* Joining Series 1 and 2 together. Also written as (3) 1, 2, 3, etc.

Year.	Compt. rend.	Dingl. poly. J.	Gazetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Pharm. Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon. scient.*	Nature.	Phil. Mag.
1860	50, 51	155-158	37, 38	79-81	4	...	19, 20
61	52, 53	159-162	39, 40	82-84	21, 22
62	54, 55	163-166	15	41, 42	85-87	23, 24
63	56, 57	167-170	16	43, 44	88-90	6	...	25, 26
64	58, 59	171-174	17	45, 46	91-93	6	...	27, 28
1865	60, 61	175-178	18	(4) 1, 2	94-96	7	...	29, 30
66	62, 63	179-182	19	3, 4	97-99	8	...	31, 32
67	64, 65	183-186	20	5, 6	100-102	9	...	33, 34
68	66, 67	187-190	21	7, 8	103-105	10	...	35, 36
69	68, 69	191-194	22	9, 10	106-108	1	11	1	37, 38
1870	70, 71	195-198	23	11, 12	(2) 1, 2	2	12	1, 2, 3	39, 40
71	72, 73	199-202	1	...	24	13, 14	3, 4	3	13	3, 4, 5	41, 42
72	74, 75	203-206	2	...	25	15, 16	5, 6	4	14	5, 6, 7	43, 44
73	76, 77	207-210	3	...	26	17, 18	7, 8	5	15	7, 8, 9	45, 46
74	78, 79	211-214	4	...	27	19, 20	9, 10	6	16	9, 10, 11	47, 48
1875	80, 81	215-218	5	...	28	21, 22	11, 12	7	17	11, 12, 13	49, 50
76	82, 83	219-222	6	...	29	23, 24	13, 14	8	18	13, 14, 15	(5) 1, 2
77	84, 85	223-226	7	...	31	25, 26	15, 16	9	19	15, 16, 17	3, 4
78	86, 87	227-230	8	...	33, 34	27, 28	17, 18	10	20	17, 18, 19	5, 6
79	88, 89	231-234	9	1	35, 36	29, 30	19, 20	11	21	19, 20, 21	7, 8
1880	90, 91	235-238	10	2	37, 38	(5) 1, 2	21, 22	12	...	1	22	21, 22, 23	9, 10
81	92, 93	239-242	11	3	39, 40	3, 4	23, 24	13	...	2	23	23, 24, 25	11, 12
82	94, 95	243-246	12	4	41, 42	5, 6	25, 26	14	1	3	24	25, 26, 27	13, 14
83	96, 97	247-250	13	5	43, 44	7, 8	27, 28	15	2	4	25	27, 28, 29	15, 16
84	98, 99	251-254	14	6	45, 46	9, 10	29, 30	16	3	5	26	29, 30, 31	17, 18
1885	100, 101	255-258	15	7	47, 48	11, 12	31, 32	17	4	6	27	31, 32, 33	19, 20
86	102, 103	259-262	16	8	49, 50	13, 14	33, 34	18	5	7	28	33, 34, 35	21, 22
87	104, 105	263-266	17	9	51, 52	15, 16	35, 36	19	6	8	29, 30	35, 36, 37	23, 24
88	106, 107	267-270	18	10	53, 54	17, 18	37, 38	20	7	9	31, 32	37, 38, 39	25, 26
89	108, 109	271-274	19	11	55, 56	19, 20	39, 40	21	8	10	33, 34	39, 40, 41	27, 28

* See footnote, p. xxii.

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1860	150	109-111	...	10, 11	13	...	39-42
61	151	112-114	...	11	14	...	43, 44
62	152	115-117	...	11, 12	Continued	...	45, 46
63	153	118-120	...	12, 13	as J.	...	47, 48
64	154	121-123	...	13	Chem. Soc.	...	49, 50
1865	155	124-126	...	14	51, 52
66	156	127-129	...	15	53, 54
67	157	130-132	...	16, 16	55, 56
68	158	133-135	...	16, 17	57, 58
69	159	136-138	...	17, 18	59, 60
1870	160	139-141	...	18, 19	61, 62
71	161	142-144	...	19, 20	63, 64
72	162	145-147	...	20, 21	65, 66
73	163	148-150	...	21, 22	67, 68
74	164	151-153	...	22, 23	69, 70
1875	165	154-156	...	23, 24	71, 72
76	166	157-159	...	24, 25	73, 74
77	167	160	...	25, 26	75, 76
78	168, 169	Continued	...	27, 28	77, 78
79	170	as Wied. Annalen.	...	28, 29, 30	79, 80
1880	171	30, 31	81, 82
81	172	31, 32, 33	83, 84
82	173	33, 34	85, 86
83	174	34, 35, 36	87, 88
84	175	36, 37, 38	89, 90
1885	176	38, 39	91, 92
86	177	40, 41	93, 94
87	178	42, 43	95, 96
88	179	43, 44, 45	97
89	180	45, 46, 47	98

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1890	12	39, 40	15	258-260	19-21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
91	13	41, 42	16	261-266	22-24	19, 20	229	24	5, 6	63, 64	8, 9	...	15	112, 113
92	14	43, 44	17	267-271	25-27	(9) 1, 2	230	25	7, 8	65, 66	10, 11	...	16	114, 115
93	15	45, 46	18	272-277	28-30	3, 4	231	26	9, 10	67, 68	12, 13	...	17	116, 117
94	16	47, 48	19	278-283	(7) 1-3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284-288	4-6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289-293	7-9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122, 123
97	19	3, 4	22	294-298	10-12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299-303	13-15	13, 14	236	31	19, 20	77, 78	22, 23	...	22	126, 127
99	21, 22	7, 8	24	304-309	16-18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310-318	19-21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
1	25, 26	11, 12	26	314-319	22-24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
2	27, 28	13, 14	27	320-325	25-27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
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4	31, 32	17, 18	29	330-337	(8) 1-3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338-343	4-6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
6	35, 36	21, 22	31	344-350	7-9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
7	37, 38	23, 24	32	351-357	10-12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	...	31	144, 145
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11	45, 46	31, 32	36	378-385	22-24	19, 20	249	44	9, 10	103, 104	48, 49	...	35	152, 153
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1890	275-278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279-282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283-286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287-290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291-294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295-298	25	17	67, 68	...	(6) 1, 2	...	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299-302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303-306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307-310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311-314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
1	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
2	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
3	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
4	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905.	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
6	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
7	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
8	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
9	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79-82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82-85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85-88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
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1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
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* See footnote, p. xxii.

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1890	A. 181	...	6	47, 48, 49	9	99	10	39-41	29	3	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42-44	30	4	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45-47	31	5	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48-50	32	6	1, 2	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51-53	33	7	3, 4, 5	...	23, 24	13-15
1895	186	...	11	57, 58, 59	14	104	15	54-56	34	8	8-10	1	24, 25	16-18
96	187, 188	...	12	59, 60	15	105	16	57-59	35	9	11, 12, 13	...	26-28	19-21
97	189, 190	...	13	60, 61, 62	16	106	17	60-63	36	10	13-15	...	28, 29	22-24
98	191	...	14	62, 63, 64	17	107	18	64-66	37	11	16-19	...	29-31	25-27
99	192, 193	...	15	64, 65, 66	18	108	19	67-69	38	12	19-22	...	31, 32	28-31
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3	200-202	4	19	71, 72	22	112	23	Physik.	42	16	33-37	9	37-39	43-46
4	203	5	20	72, 73, 74	23	113	24		43	17	38-42	10	39, 40	47-49
1905	204, 205	6	21	74-76	24	114	25		44	18	43-48	11	40-42	50-53
6	206	7	22	A, 77, 78	25	115	26		45	19	48-52	12	42, 43	54-57
7	207	8	23	78, 79, 80	26	116	27		46	20	52-56	13	43, 44	58-60
8	207-209	9	24	80, 81	27	117	28		47	21	56-60	14	44-46	61-64
9	209, 210	10	25	82, 83	28	118	29		48	22	61-65	15	46, 47	65-69
1910	210	11	26	83, 84	29	119	30		49	23	65-69	16	48, 49	70-74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69-73	17	49, 50	75-77
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13	212, 213	14	29	88, 89	32	122	33		52	26	79-83	19	52, 53	81-86
14	213, 214	15	30	89, 90	33	123	34		53	27	84-90	20	54	86-88
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* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF
INORGANIC CHEMISTRY.
VOLUME VI. PART V.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. VI. PART V. ANTIMONY AND BISMUTH.

CHAPTER I.

ANTIMONY AND ITS ALLOYS.

Symbol, Sb. Atomic Number, 51. Atomic Weight, 121.76 (O = 16).

Occurrence.—The principal ores of antimony contain the mineral known variously as *stibnite*, *antimonite* or *antimony glance*, Sb_2S_3 . Stibnite is found principally in France,¹ Italy, Algeria and China, and to a smaller extent in Czechoslovakia, Spain, Portugal and Japan. In India, stibnite lodes in gneissose granite occur in the Punjab, and with cervantite in the Northern Shan states, while the tetrahedrite in Slesmanabad copper lodes is highly antimonial. The ores frequently contain gold, silver and arsenic, and are associated with galena, iron pyrites, spathic iron ore, quartz, calcite and barytes.

Other antimony minerals occasionally found in ores that are commercially valuable include *cervantite* or *antimony ochre*, Sb_2O_3 , *kermesite*, $2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$, *valentinite*, *white antimony* or *antimony bloom*, Sb_2O_3 (rhombic), and *senarmontite*, Sb_2O_3 (cubic).

Native antimony occurs in too small quantity to be commercially valuable.²

Many other antimony minerals have been described. These are mainly complex sulphide minerals which may be regarded as thioantimonites or thioantimonates, oxidised minerals which may be antimonites or antimonates, and a few miscellaneous minerals difficult to classify. In the following list the formulæ ascribed to the various minerals are intended to convey the approximate composition of the mineral; it is not suggested that they represent definite chemical compounds in all cases.³

Antimony has also been found in animal tissues.⁴

¹ Charrin, *Génie civil*, 1932, 100, 314.

² Wang, "Antimony" (Griffin, 1919), p. 46.

³ In addition to the literature cited, reference may also be made to Shannon, *Amer. Mineral.*, 1918, 3, 23; Schaller, *Bull. U.S. Geol. Survey*, 1916, 610, 104; Halse, "Antimony Ores, Monograph on Mineral Resources with Special Reference to the British Empire" (Murray, 1925); Voskuil, "Minerals in Modern Industry" (Wiley and Sons, 1930), p. 260.

⁴ Chapman, *Nature*, 1930, 126, 761.

MINERALS CONTAINING ANTIMONY.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Native antimony .	Chief impurities: silver, iron and arsenic	Rhombohedral: $a : c = 1 : 1.32362$	3 to 3.5	6.65 to 6.72	..	Dana,* p. 12; C. H. Behre, <i>Amer. J. Sci.</i> , 1921, [5], 2, 330.
Stibnite, or Anti- monite.	Sb_2S_3	Rhombic: $a : b : c =$ 0.99257 : 1 : 0.338 (see p. 100)	2	4.52 to 4.62	Germany, France, Italy, Spain, Yugoslavia, Czechoslovakia, Por- tugal, Scotland, Corn- wall, Mexico, Algeria, Borneo, India, Aus- tralia, Japan, China, U.S.A.	Dana, p. 36. App. II, p. 99; P. Gravano, <i>Atti R. Accad. Lincei</i> , 1926, [6], 3, 310; L. Marie, <i>Archiv Hemijnu</i> , 1930, 4, 142.
Guejarite .	$Cu_3S_2Sb_2S_3$	Rhombic: $a : b : c =$ 0.8221 : 1 : 0.7841	3.5	5.03	Sierra Nevada, Anda- lusia	Dana, p. 110.
Chalcostibite .	$Cu_3S.Sb_2S_3$	Rhombic: $a : b : c =$ 0.5283 : 1 : 0.6234	3 to 4	4.75 to 5.0	Harz, Spain	Dana, p. 113.
Wolfsbergite .	$CuSbS_2$	Rhombic: $a = 6.01$ A. $b = 3.78$ A. $c = 14.46$ A. Unit cell contains 4 molecules	W. Hofmann, <i>Zeitsch.</i> <i>Kryst.</i> , 1933, 84, 177.

* Dana. J. D. and E. S. Dana, "A System of Mineralogy" (London and New York), 6th Ed., 1899.
 Dana, App. I. *Ibid.*, Appendix I, 1899.
 Dana, App. II. *Ibid.*, Appendix II, 1909.
 Dana, App. III. *Ibid.*, Appendix III, 1919.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Falkenhaynite .	$3\text{Cu}_2\text{S.Sb}_2\text{S}_3$	Massive	..	4.83	Joachimstal	Dana, p. 1034.
Tetrahedrite .	$4\text{Cu}_2\text{S.Sb}_2\text{S}_3$	Cubic, tetrahedral	3 to 4.5	4.75 to 5.0	Cornwall, Germany, Tyrol, Czechoslovakia, Jugoslavia, S. America	Dana, p. 137.
Bournonite .	$3(\text{Cu}_2, \text{Pb})\text{S.Sb}_2\text{S}_3$	Rhombic: $a:b:c =$ 0.9380 : 1 : 0.8969	2.5 to 3.0	5.7 to 5.9	Harz, Czechoslovakia, Jugoslavia, Italy, Cornwall, Mexico, S. America	Dana, p. 126.
Stylopyrite .	$3(\text{Cu}_2, \text{Ag}_2, \text{Fe})\text{S.Sb}_2\text{S}_3$	Rhombic	3	4.79	Chile	Dana, p. 130.
Eichbergite .	$(\text{Cu}, \text{Fe})_2\text{S}_3(\text{Bi}, \text{Sb})_2\text{S}_3$..	> 6	5.36	Austria	Dana, App. III, p. 26.
Goldfieldite .	$3\text{Cu}_2\text{S}(\text{Sb}, \text{Bi}, \text{As})_2(\text{S}, \text{Te})_3$	Non-crystalline	3 to 3.5	..	Nevada	Dana, App. III, p. 34.
Livingstonite .	$\text{HgS.2Sb}_2\text{S}_3$	Prismatic	2	4.81	Mexico	Dana, p. 109.
Pyargyrite .	$3\text{Ag}_2\text{S.Sb}_2\text{S}_3$ (Sb 22.13 per cent. Ag 58.81 per cent. S 17.40 per cent.)	Rhombohedral, hemimorphic: $a:c = 1:0.7892$	2.5	5.85	Germany, Czechoslovakia, Jugoslavia, Norway, Spain, Cornwall, Mexico, U.S.A., S. America	Dana, p. 131; C. Castro, <i>Bol. Min. Mexico</i> , 1919, 7, 275.
Miargyrite .	$\text{Ag}_2\text{S.Sb}_2\text{S}_3$	Monoclinic: $a:b:c =$ 2.9945 : 1 : 2.9095, $\beta = 81^\circ 22' 35''$	2 to 2.5	5.1 to 5.3	Saxony, Czechoslovakia, Spain, Mexico, Chile	Dana, p. 116.
Pyrostilpnite .	$3\text{Ag}_2\text{S.Sb}_2\text{S}_3$	Monoclinic: $a:b:c =$ 0.3646 : 1 : 0.1782, $\beta = 90^\circ$	2	4.2 to 4.25	Germany, Czechoslovakia	Dana, p. 135.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Stephanite .	$5\text{Ag}_3\text{Sb}_2\text{S}_3$	Rhombic, hemimorphic: $a:b:c = 0.6291:1:0.6851$	2 to 2.5	6.2 to 6.3	Germany, Czechoslovakia, Yugoslavia, Norway, Cornwall, Mexico, S. America, Nevada	Dana, p. 143.
Polybasite .	$9\text{Ag}_3\text{Sb}_2\text{S}_3$	Rhombic: $a:b:c = 0.5793:1:0.9130$	2 to 3	6.0 to 6.2	Saxony, Czechoslovakia, Mexico, Chile, U.S.A.	Dana, p. 146.
Polyargyrite .	$12\text{Ag}_3\text{Sb}_2\text{S}_3$	Cubic	2.5	7.0	Baden	Dana, p. 146.
Brongniardite .	$\text{Ag}_2\text{S.PbS.Sb}_2\text{S}_3$	Cubic	> 3	5.95	Mexico	Dana, p. 123.
Diaphorite .	$5(\text{Ag}_2, \text{Pb})\text{S.2Sb}_2\text{S}_3$	Rhombic: $a:b:c = 0.4919:1:0.7345$	2.5 to 3.0	5.9 to 6.0	Saxony	Dana, p. 124.
Freieslebenite .	$5(\text{Ag}_2, \text{Pb})\text{S.2Sb}_2\text{S}_3$	Monoclinic: $a:b:c = 0.5871:1:0.9277$, $\beta = 87^\circ 48'$	2 to 2.5	6.2 to 6.4	Saxony, Yugoslavia, Spain, Colorado	Dana, p. 124.
Andorite (also Sundite and Webnerite)	$\text{Ag}_2\text{S.2PbS.3Sb}_2\text{S}_3$	Rhombic: $a:b:c = 0.6772:1:0.4458$	3 to 3.5	5.50	Jugoslavia	Dana, App. I, p. 4.
Samsonite .	$2\text{Ag}_3\text{S.MnS.Sb}_2\text{S}_3$	Monoclinic: $a:b:c = 1.2777:1:0.8192$, $\beta = 87^\circ 18'$	Harz	Dana, App. III, p. 69.
Jamesonite .	$2\text{PbS.Sb}_2\text{S}_3$ (with iron, silver, copper and zinc)	Rhombic: $a:c = 0.8915:1$	2 to 3	5.5 to 6.0	Cornwall, Siberia, Jugoslavia, Spain, Brazil	Dana, p. 122.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Zinkenite .	$\text{PbS.Sb}_2\text{S}_3$	Rhombohedral: $a : b : c =$ $0.5575 : 1 : 0.6353$	3 to 3.5	5.30 to 5.35	Germany, France, U.S.A.	Dana, p. 112.
Plagionite .	$5\text{PbS.4Sb}_2\text{S}_3$	Monoclinic: $a : b : c =$ $1.1331 : 1 : 0.4228,$ $\beta = 72^\circ 50'$	2.5	5.4	Germany	Dana, p. 118.
Warrenite .	$3\text{PbS.2Sb}_2\text{S}_3$	Acicular	Colorado	Dana, p. 120.
Kobellite .	$2\text{PbS. (Bi, Sb)}_2\text{S}_3$	Massive (resembling stilbite)	2.5 to 3	6.29 to 6.32	Sweden, Colorado	Dana, p. 123.
Samseyite .	$7\text{PbS.3Sb}_2\text{S}_3$	Monoclinic: $a : b : c =$ $1.4442 : 1 : 1.1051,$ $\beta = 71^\circ 4'$	Jugoslavia	Dana, p. 123.
Boulangerite .	$5\text{PbS.2Sb}_2\text{S}_3$	Rhombohedral: $a : b : c =$ $0.5527 : 1 : 0.7478$	2.5 to 3	5.75 to 6.0	France, Lapland, Harz, Czechoslovakia, Tuscany, Nevada	Dana, p. 129; App. I, p. 11.
Menghinite .	$4\text{PbS.Sb}_2\text{S}_3$	Rhombohedral: $a : b : c =$ $0.5289 : 1 : 0.3632$	2.5	6.34 to 6.43	Tuscany, Saxony, Canada	Dana, p. 142.
Geocrinite .	$5\text{PbS.Sb}_2\text{S}_3$	Rhombohedral: $a : b : c =$ $0.5805 : 1 : 0.5028$	2.5	6.3 to 6.45	..	Dana, p. 143.
Kilbriekenite .	$6\text{PbS.Sb}_2\text{S}_3$	Massive	..	6.4	Iceland	Dana, p. 145.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Rathite .	Probably a complex thio- antimonite (S 23.72; As 17.24; Sb 4.53; Pb 52.98; Fe 0.56)	Rhombic: $a : b : c =$ 0.6681 : 1 : 1.0579	Switzerland	Dana, App. I, p. 58.
Berthierite .	$\text{FeS.Sb}_2\text{S}_3$	Elongated prisms	2 to 3	4 to 4.3	France, Saxony, Corn- wall, Jugoslavia, Cali- fornia, New Bruns- wick	Dana, p. 114.
Cylindrite .	$3\text{PbS.Sb}_2\text{S}_3 + 3(\text{PbS.2SnS}_2)$	Massive	2.5 to 3	5.42	Bolivia	Dana, App. I, p. 21.
Franckeite .	$2\text{PbSnS}_3.\text{Pb}_3\text{Sb}_2\text{S}_6$	Massive	2.75	5.55	Bolivia	Dana, App. I, p. 26.
Famatinite .	$3\text{Cu}_2\text{S.Sb}_2\text{S}_3$	Rhombic	3.5	4.57	S. America	Dana, p. 149.
Vrbaite .	$\text{TeAs}_2\text{SbS}_6$	Rhombic: $a : b : c =$ 0.5659 : 1 : 0.4836	3.5	5.3	Macedonia	Dana, App. III, p. 83.
Epiboulangerite .	$3\text{PbS.Sb}_2\text{S}_3$	Rhombic	..	6.3	Silesia	Dana, p. 149.
Kermesite .	$2\text{Sb}_2\text{S}_3.\text{Sb}_2\text{O}_3$	Rhombic or Mono- clinic: $a : b : c =$ 3.9650 : 1 : 0.8535, $\beta = 90^\circ 0'$	1 to 1.5	4.5 to 4.6	Saxony, Scotland, Jugo- slavia	Dana, p. 106.
Corynite .	Ni(As, Sb)S	Cubic	4.5 to 5	5.994	Carinthia	Dana, p. 91.
Ullmannite .	NiSbS	Cubic	5.0 to 5.5	6.2 to 6.7	Germany	Dana, p. 91.
Wolfachite .	Ni(As, Sb)S	Rhombic	4.5 to 5	6.372	Baden	Dana, p. 102.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Nagyagite .	Thielluride of lead containing antimony and gold	Rhombic: $a:b:c = 0.2810:1:0.2761$	1 to 1.5	6.85 to 7.2	Transylvania	Dana, p. 105.
Silberphyllinglanz	Contains antimony, lead, tellurium, gold, silver and sulphur	..	1.2	5.8 to 5.9	..	Dana, p. 106.
Bolivianite .	Antimonial silver sulphide	Rhombic	2.5	4.82	Bolivia	Dana, p. 107.
Plumbostannite .	Contains antimony, tin, lead, iron, zinc and sulphur	Amorphous	..	4.5	Peru	Dana, p. 108.
Histrixite .	$7\text{Bi}_2\text{S}_3.2\text{Sb}_2\text{S}_3.5\text{CuFeS}_2$	Rhombic	2	Dana, App. II, p. 52.
Senarmonite .	Sb_3O_3	Cubic: $a = 11.14 \text{ \AA}$.	2 to 2.5	5.22 to 5.30	Algeria, Hungary, Cornwall, Canada	Dana, p. 198; R. M. Bozorth, <i>J. Amer. Chem. Soc.</i> , 1923, 45, 1621.
Valentinite .	Sb_2O_3	Rhombic: $a:b:c = 0.3910:1:0.3364$	2.5 to 3	5.566	Saxony, Algiers, Canada, Czechoslovakia, Yugoslavia	Dana, p. 199.
Partzite .	Hydrated antimony trioxide, with other metallic oxides	..	3 to 4	3.8	California, Peru	Dana, p. 204.
Cervantite .	Sb_2O_4	Rhombic	4 to 5	4.084	Spain, Yugoslavia, Tuscany, Cornwall, Scotland, Borneo, Mexico, Canada, U.S.A.	Dana, p. 203.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Stibiconite .	$\text{Sb}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Massive, compact	4 to 5.5	5.1 to 5.28	Bavaria, Borneo, Mexico, Peru	Dana, p. 203.
Stibianite .	$\text{Sb}_2\text{O}_3 \cdot \text{As}$	Massive, porous	5	3.67	Australia	Dana, p. 203.
Stetefeldite .	Sb_2O_3 (with oxides of copper and iron, and water)	..	3.5 to 4.5	4.12 to 4.24	Nevada	Dana, p. 204.
Volgerite .	$\text{Sb}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	Massive	Algeria	Dana, p. 203.
Rivotite .	Oxides of antimony, silver, copper and car- bon, with lime	Amorphous, com- pact	Lerida	Dana, p. 203.
Stibioferrite .	Oxides of antimony, iron and silicon, with water	Amorphous	4	3.598	U.S.A.	Dana, p. 204.
Barconite .	Sb 50.11; S 2.82; Hg 20.75; Ca 3.88; O 17.61; H_2O 4.73	Massive	5.5	5.343	Mexico	Dana, p. 866.
Langbanite .	Antimony, iron, man- ganese, silicon, oxygen	Hexagonal, tabular crystals	Dana, p. 1039.
Chondrostibian .	Antimony, arsenic, man- ganese, iron, oxygen and water	Cubic (?)	Sweden	Dana, App. I, p. 17.
Nadorite .	$\text{PbSb}_2\text{O}_4 \cdot \text{PbCl}_2$	Rhombic: $a : b : c =$ 0.7490 : 1 : 1.0310	3.5 to 4	7.02	Algiers	Dana, p. 863.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Melanostibian	Antimonite of ferrous iron and manganese	Massive	4	..	Sweden	Dana, App. I, p. 45.
Amniolite	An impure antimonite of copper	Earthy powder	Chile	Dana, p. 865.
Atopite	$2\text{CaO} \cdot \text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ($x = 6$ to 8)	Cubic: $a = 10.26$ A. Unit cell contains 8 molecules	5.5 to 6	5.03 to 5.32	Sweden	Dana, p. 861; G. Natta and M. Baccaredda, <i>Atti R. Accad. Lincei</i> , 1932, 15, 389.
Romeite	$3\text{CaO} \cdot 2\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ($x = 6$ to 8)	Cubic: $a = 10.26$ A. Unit cell contains 4 molecules	5.5	4.71 to 5.07 4.98 (calc.)	Piedmont	Dana, p. 862; Natta and Baccaredda, <i>loc. cit.</i> ; O. Seitzler, <i>Zeitsch. Krist.</i> , 1932, 81, 253.
Galicia ochre	$3\text{CaO} \cdot 2\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ($x = 6$ to 8)	Cubic: $a = 10.25$ A. Unit cell contains 4 molecules	..	4.30 5.00 (calc.)	..	Natta and Baccaredda, <i>loc. cit.</i>
Cordova ochre	$5\text{CaO} \cdot \text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ($x = 6$ to 8)	Cubic: $a = 10.25$ A. Unit cell contains 8 molecules	..	4.21 4.66 (calc.)	..	<i>Ibid.</i>
China ochre	$5\text{CaO} \cdot 4\text{Sb}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ($x = 6$ to 8)	Cubic: $a = 10.25$ A. Unit cell contains 2 molecules	..	4.44 4.82 (calc.)	..	<i>Ibid.</i>
Lewisite	$5\text{CaO} \cdot 2\text{TiO}_2 \cdot 3\text{Sb}_2\text{O}_3$	Cubic	..	4.529	..	Dana, App. I, p. 42.
Mauzeilite	Titano-antimonate of cal- cium and lead	..	6 to 6.5	5.11	Sweden	<i>Ibid.</i> , p. 45.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Bindheimite .	Hydrated antimonate of lead	Amorphous	4	4.60 to 4.76	Siberia, Cornwall, U.S.A.	Dana, p. 862.
Ochrolite .	$\text{Pb}_4\text{Sb}_2\text{O}_7 \cdot 2\text{PbCl}_2$	Rhombic: $a : b : c =$ 0.9050 : 1 : 2.0137	Sweden	Dana, p. 864.
Arequipite .	Probably a silico-anti- monate of lead	Compact, wax-like	6	..	Peru	Dana, p. 865.
Coronguite .	Antimonate of lead and silver	Amorphous, earthy	2.5 to 3	5.05	Peru	Dana, p. 866.
Tazmite .	An impure arsenio-anti- monate of bismuth	Amorphous, earthy, fibrous	Bolivia	Dana, p. 866.
Bastilite .	Hydrated antimonate of iron and manganese	Sweden	..
Lamprostibian .	Probably a hydrated antimonate of iron and manganese	..	4	..	Sweden	Dana, App. I, p. 40.
Magnetostibian .	A complex antimonate of iron and manganese, with arsenic	Sweden	Dana, App. I, p. 44.
Tripihyite .	Probably $2\text{FeO} \cdot \text{Sb}_2\text{O}_3$	Micro-crystalline	..	5.82	..	Dana, App. I, p. 70.
Derbylite .	$\text{FeO} \cdot \text{Sb}_2\text{O}_3 + 5\text{FeO} \cdot \text{TiO}_2$	Rhombic: $a : b : c =$ 0.9661 : 1 : 0.5502	5	4.512 to 4.530	Brazil	Dana, App. I, p. 22.

Name.	Composition.	Crystalline Form.	Hardness (Mohs' Scale).	Density.	Locality.	References.
Flajolite .	$4\text{FeSbO}_4 \cdot 3\text{H}_2\text{O}$	Compact or earthy	Algeria	Dana, App. III, p. 30.
Horsfordite .	Probably Cu_6Sb	Massive	4 to 5	8.812	Asia Minor	Dana, p. 44.
Dyscrasite .	Ag_3Sb (perhaps a mixture of Ag_3Sb and Ag_6Sb)	Rhombic: $a : b : c =$ 0.5775 : 1 : 0.6718	3.5 to 4	9.44 to 9.85	Baden, Harz, France, Spain, Bolivia	Dana, p. 42; G. M. Schwarz, <i>Amer. Mineral.</i> , 1928, 13, 495.
Stibiotantalite .	$(\text{SbO})_3(\text{Ta}, \text{Nb})_2\text{O}_6$	Rhombic: $a : b : c =$ 0.7995 : 1 : 0.8448	5 to 5.5	5.98 to 7.37	California	Dana, App. I, p. 64; App. II, p. 98; App. III, p. 74; W. E. Ford, <i>Amer. J. Sci.</i> , 1911, [4], 32, 287.
Breithauptite .	NiSb	Hexagonal: $a : c = 1 : 0.8586$	5.5	7.541	Harz	Dana, pp. 72, 1029; App. I, p. 11.
Haueckornite .	$(\text{Ni}, \text{Co})_4(\text{S}, \text{Sb}, \text{Bi})_8$	Tetragonal: $a : c = 1 : 1.05215$	Prussia	Dana, App. I, p. 33.
Willyamite .	CoSbS.NiSbS or $\text{CoS}_2.\text{NiS}_2.\text{CoSb}_2.\text{NiSb}_2$	Cubic	5.5	6.87	Broken Hill, New South Wales	Dana, App. I, p. 73.
Thrombolite .	Probably a mixture. CuO 39.44 Fe_2O_3 1.05 Sb_2O_3 6.65 Sb_2O_5 32.52 H_2O 16.56	Amorphous	..	3.67	Hungary	Dana, p. 1050.
Allemontite .	SbAs_3 Sb 34.8; As 65.2	Rhombohedral	3.5	6.203	Bohemia, Styria, Harz	Dana, p. 12.

Early History.—There can be little doubt that antimony was known in ancient times, either in the form of the metal or in compounds. The Chinese were acquainted with the metal five thousand years ago; and certain references in the Old Testament (II Kings, 9, 30; Ezekiel, 23, 40; Jeremiah, 4, 30) have been considered by most commentators to refer to stibnite or sulphide of antimony.

Ancient bronzes discovered by archæologists in many parts of the world have been found to contain antimony; a vase found by M. de Saizec at Tells in Chaldea consisted of almost pure antimony;¹ and an Egyptian copper ewer and basin of the Fifth or Sixth Dynasty has been shown to be plated with antimony.²

It has been suggested that the knowledge of antimony passed from the East through Arabia into Europe by the agency of the Arabic chemist Djaber or Geber, who lived in the eighth century. References to antimony in the literature of the Middle Ages are extremely confusing, however, and it is not until towards the end of the sixteenth century that the obscurity is dispersed.³ Robert Boyle⁴ was clearly familiar with the starred appearance of the cast metal, to which he refers as "the starry regulus of Mars and antimony" (see Plate).

The confusion which exists with regard to the early history of antimony is to a great extent due to the ambiguity of the origin and meaning of the words *antimonium* and *stibium*. Both words appear to have been employed to indicate in some cases the metal, in others the sulphide mineral *stibnite*. In addition, the metal itself was regarded by some authorities as a semi-metal, by others as a mixture of metals.

In Arabic writings the mineral stibnite is referred to as *kohl*, a word which is still retained, with a very different meaning, in *alcohol*. This term "alcohol" is used for stibnite in some Latin writings, but is more frequently found in the Spanish. The more usual Latin term was *stibium*. The origin of the term *antimonium* is more difficult to trace. The fable that it arose from the accidental poisoning of some monks may be dismissed on linguistic grounds. The word was used by Basil Valentine; and as in the original copy of his work (which was written in German) it always appears in italics, it is probably of Latin origin. This view is supported by the fact that one of the earliest recorded instances of the use of the word is in the Latin writings of Geber, who wrote in the thirteenth century. (This author is not to be confused with the Arabic chemist with a similar name, who flourished in the eighth century.) The word *stibium* appears to have been more generally employed, although both words survived until the time of Lavoisier; both were used indiscriminately to describe the metal and stibnite. An account of the available knowledge of antimony up to the beginning of the seventeenth century is to be found in the works of Basil Valentine.⁵

¹ M. Berthelot, *Compt. rend.*, 1887, 104, 265.

² C. G. Fink and A. H. Kopp, *Metropolitan Museum Studies*, 1933, 4, 163.

³ A. Libavius, "*Alchymia*" (Frankfurt, 1595; 2nd Ed., 1606).

⁴ Boyle, "On the Unsuccessfulness of Experiments," *Opera*, 1772, i, 325.

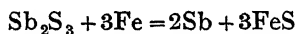
⁵ Dyson, *Pharm. J.*, 1928, [4], 67, 397. See also Valentine, "*The Triumphant Chariot of Antimony*," English Translation (London, 1661); Pliny, *Historia naturalis*, 33, 34; Dioscorides, *De materia medica*, 5, 49; Agricola, "*De re metallica*" (Basiliæ, 1556), English Translation (London, 1912), p. 428; Ecker, "*Beschreibung aller fürnemsten mineralische Erztz und Berckwercksarten*" (Prag, 1574); Sala, "*Anatomia antimonii*" (Francofurti, 1617); A. von Suchten, "*Mysteria gemina antimonii*" (Nürnberg, 1680); *Chymische Schriften* (Frankfurt, 1680), pp. 229, 267; Lemery, "*Traité de l'antimoine*" (Paris, 1707); Kunckel, "*Vollständiges Laboratorium chymicum*" (Berlin, 1716); Morhof,



The Macro-structure of Antimony.

Antimony compounds were largely employed in medicinal preparations in the Middle Ages. Paracelsus was one of the first to use them, having made *butter of antimony* (antimony trichloride) by distilling corrosive sublimate with antimony sulphide. Treatment with water yielded *mercurius vitæ* (an oxychloride)—a preparation that was popularised by the Veronese physician Algarotus or Algaroth, and hence became known as "*Powder of Algaroth*." Sulphide of antimony was itself used considerably for a time, but was practically discontinued after considerable discussion by the medical profession. Tartar emetic, the most widely employed antimony compound, was also probably used in early times. In ancient times wine was permitted to stand overnight in antimony goblets, and was taken medicinally on the following day. This practice persisted up to the time of Boyle, but was then superseded by the introduction of metallic pills of antimony.¹

Extraction.²—Antimony is extracted mainly from ores containing antimony trisulphide in the form of stibnite. Rich ores are first subjected to liquation, whereby the fusible sulphide is removed from the gangue and concentrated. The concentrate is then reduced to metal by smelting with wrought iron in pots, in reverberatory furnaces or sometimes in blast furnaces,³



The reduction in pots is carried out in three stages: (1) A mixture of liquated ore, wrought iron and common salt is fused together and a crude product obtained containing about 90 per cent. antimony and 7 to 8 per cent. iron; (2) this is again remelted with more liquated ore and common salt, the bulk of the iron being thereby removed; (3) finally this second product is remelted with a special flux made by fusing together three parts of commercial potassium carbonate with two parts of liquated ore.

The reduction in reverberatory furnaces is carried out in two stages: (1) Fusion of liquated ore with scrap iron to produce crude metal, and (2) refining the crude metal. In the first stage the liquated ore is smelted with a flux containing soda ash, salt cake and common salt. This results in the production of a slag of low density containing sulphide of iron and sulphide of sodium, from which the crude antimony can settle fairly readily. The crude product contains 94 to 95 per cent. antimony mixed with iron, sulphur, lead and arsenic. This is refined by melting carefully under a flux of sodium carbonate. After a time the impurities can be skimmed off and then a mixture containing antimony oxide, antimonyl sulphide, sodium carbonate and a little coal is added. The refined metal is then ladled out and cast as "*star antimony*," the surface of the cakes showing a well-defined crystal

Polyhistor (Lübeck, 1714), i, 84; Litré, *Dictionnaire de la Langue française* (Paris, 1873), i, 156; Helm and Hilprecht, *Chem. Zeit.*, 1901, 25, 250; Hommel, *Zeitsch. angew. Chem.*, 1912, 25, 97; *Chem. Zeit.*, 1912, 36, 918; Hyman, *Chem. and Ind. Review*, 1924, 2, 1006; Auden, *ibid.*, 1132.

¹ Dyson, *loc. cit.*, pp. 520, 596.

² Wang, *loc. cit.*, p. 67; Gowland, "*The Metallurgy of the Non-Ferrous Metals*" (Griffin), p. 565. See also Wang, *Proc. World Eng. Congr. Tokyo*, 1929, 1931, 35, 185; *Engineering*, 1929, 128, 726; Brazenall, *Chem. Eng. Mining Rev.*, 1932, 24, 312, 341; Tafel, *Metall und Erz*, 1931, 28, 503; Kai Ho, *Science (China)*, 1933, 17, 16.

³ Schoeller, *Trans. Inst. Min. Met.*, 1918, 27, 237; Brazenall, *The Chemical Age, Metallurgical Section*, 1932, 27, 12.

structure. A method has also been suggested for refining electrolytically¹ using an electrolyte containing antimony trifluoride with about 100 grams of free sulphuric acid and 20 grams of free hydrofluoric acid per litre.

Low-grade ores, which generally contain oxidised minerals in addition to sulphides, are first roasted to produce either the non-volatile tetroxide or the volatile trioxide. With oxidised ores recovery of antimony is incomplete unless anthracite is added to the charge. Thus, treated at 900° C. without anthracite, only the antimony present as sulphide is recovered, while with anthracite almost complete recovery has been effected. Using an ore containing 3.3 per cent. antimony, partly sulphidic and partly oxidised, the average anthracite consumption was 15 to 20 per cent. of the charge, of which 5 to 8 per cent. was used as reducer and 10 to 12 per cent. as fuel.² The oxides obtained are reduced to metal by carbon in crucibles or reverberatory furnaces, using an alkaline flux containing soda ash, salt cake and common salt.

For roasting sulphide ores two methods are used, viz., simple roasting yielding mainly antimony tetroxide, and volatilisation roasting yielding mainly antimony trioxide. In the former, reverberatory furnaces are employed, the flue gases passing through a condensing plant for the recovery of any antimony trioxide that may be formed. For volatilisation roasting either the Herreschmidt or the Chatillon process is used. In the Herreschmidt process, the furnace is a rectangular shaft of firebrick with fire-bars arranged in steps. The gases from this furnace are cooled by passing them through a series of iron pipes into a wooden tower packed with coke down which water trickles. The water is collected at the bottom of the tower in tanks in which the oxide is allowed to settle. In the Chatillon process a double cupola type of furnace is employed. The flue gases containing volatilised oxide pass through a condensing plant (which consists of sheet iron tanks so disposed that the flue gases can pass all round them), and are then forced into a filtration chamber which is fitted with bags of coarse cotton canvas or of woollen material.

The volatilisation and oxidation of antimony trisulphide have been studied in detail.³ From the results it is suggested that rich or concentrated ores which do not contain precious metals, arsenic or lead should be roasted to antimony tetroxide, while poorer ores, and ores containing precious metals, should be roasted to antimony trioxide. It is further suggested that it is inadvisable to extract antimony from rich ores by fusing the sulphide with iron on account of the high fusion temperature required; if this process is adopted a reducing atmosphere should be employed and the dust in the flue gases recovered.

The reduction of oxides of antimony may also be effected by the action of arsenic on fused sodium hydroxide in the presence of the oxide.⁴

Various wet methods for the extraction of antimony have been suggested but do not appear to have been successful.⁵ Electrolytic

¹ Roscher, *U.S. Patent*, 1930, 1780944.

² Slobodska, *Tsvetnue Metal.*, 1932, Nos. 7-8, 108.

³ Shakov and Slobodska, *Tsvet. Met.*, 1930, 1294; *Chimie et Industrie*, 1931, 25, 1126. See also this Volume, pp. 101, 102.

⁴ *French Patent*, 1930, 694283.

⁵ Coolbaugh and Read, *U.S. Patent*, 1926, 1597018. See also Wang, *loc. cit.*; Gowland, *loc. cit.*

methods have, however, been developed and it is claimed that compact antimony of great purity can be obtained by these methods.^{1, 2}

Chemically pure antimony has been prepared³ by converting antimony trichloride, purified by distillation, into chlorantimonic acid, which, after purification by recrystallisation, is hydrolysed to antimonious acid. The antimonious acid is finally reduced to metal by fusion with potassium cyanide.

The production of "secondary antimony" (*i.e.* the recovery of antimony from alloys and residues) forms an important means of obtaining the metal. In the United States of America in 1928, between 170,000 and 180,000 tons of old lead accumulators containing 3 per cent. antimony were available.⁴ For the treatment of lead-antimony alloys the Harris process is largely employed in England and some other countries.⁵ In this process the scrap metal is melted with an oxidising alkaline flux. Arsenic, antimony and tin are then removed by skimming as sodium arsenate, antimonate and stannate. The sodium antimonate is separated from these by lixiviation, and is reduced to antimony by treatment with carbonaceous material.⁶ In another method that has been suggested, the alloy is treated with metallic sodium in order to form an alloy of sodium and antimony. This is dissolved in molten caustic soda, and the antimony separated by treatment with water.⁷

More than three-quarters of the world's supply of antimony ore are obtained from the province of Hunan, China. In France, the ore deposits at La Lucette yield an annual production of 3,000 tons of antimony.⁸ About 1,000 tons of antimonial lead, containing 21 per cent. antimony, are also produced annually in Burma.⁹ The total world production of antimony ore, returned as tons of metal content, is given in the following table :—¹⁰

	1926.	1927.	1928.	1929.	1930.	1931.
Long Tons	31,400	30,000	30,000	31,000	23,000	27,000

Physical Properties of Antimony.

Numerous varieties of antimony have been described by various workers, but the existence of definite *allotropic forms*, and their relationship to one another, have not yet been fully established. According

¹ Engelhardt, *Zeitsch. Elektrochem.*, 1931, 37, 813; Izgaruishev and Pletenev, *ibid.*, 365; van Erckelens, *Eng. Mining J.*, 1931, 132, 160.

² Katz, "*Mineral Resources of the United States, 1927*" (Washington, Government Printing Offices, 1930), p. 40. See also *Eng. Mining J.*, 1927, 123, 432; Vogel, *Metallbörse*, 1930, 20, 537, 651.

³ Groschuff, *Zeitsch. anorg. Chem.*, 1918, 103, 164.

⁴ Wilson, *Metal Industry (New York)*, 1930, 28, 162.

⁵ Bruchhold, *Bol. minero*, 1929, 28, 191; Winter, *Eng. Mining J.*, 1928, 125, 893, 969; *French Patent*, 1928, 665174; Kirsebom, *British Patent*, 1928, 315811; Short, *Metal Industry (London)*, 1929, 34, 42.

⁶ See also Vogel, *Metallbörse*, 1929, 19, 2441, 2499, 2555.

⁷ Hanak, *U.S. Patent*, 1930, 1786908.

⁸ Charrin, *Génie civil*, 1932, 100, 314.

⁹ Pascoe, *Records Geol. Survey India*, 1930, 64, 26.

¹⁰ "*Mineral Resources of the British Empire and Foreign Countries*," Statistical Summary (London, H.M.S.O., 1933), p. 27. For a review of the antimony industry from 1913-1933, see Kai Ho, *Science (China)*, 1933, 17, 16.

to Cohen and his co-workers,¹ two forms of antimony, α and β , can exist. α , or *rhombohedral antimony*, is more stable than β , *amorphous* or *explosive antimony*, at all temperatures below the melting point.² A very unstable yellow modification has also been described.³

Irregularities in the dilatometric curve at 96° C. and 101° C. were formerly taken to indicate allotropic transformations,⁴ but it is probable that they are due to mechanical deformation. Similar irregularities in the electrical resistance curve disappeared after tempering at 600° C., and X-ray observations taken at room temperature, 150° C. and 200° C., indicated no change in structure.⁵

Rhombohedral Antimony or α -Antimony is the ordinary form of the element. It is a white, lustrous metal, crystallising in the rhombohedral class of the rhombohedral division of the hexagonal system⁶

$$a : c = 1 : 1.8286, \quad \alpha = 86^\circ 58'$$

From X-ray analysis it is deduced that the structure consists of two interpenetrating face-centred lattices, the symmetry being that of a rhombohedron. The unit rhomb contains eight atoms; the length of the edge of a unit rhomb is 6.20 Å., and the shortest distance between two atoms 2.92 Å. The angle between any two edges of the rhombohedron is $86^\circ 58'$, and the angle between the (100) and (010) faces is $92^\circ 53'$. There is very perfect cleavage at right-angles to the trigonal axis and parallel to the (111) planes, and a less perfect cleavage parallel to the (110) planes.⁷ The crystal forms of electrolytic antimony,⁸ and of native antimony,⁹ have also been investigated.

The density¹⁰ is 6.684 at 25° C.; that calculated from X-ray data¹¹ is 6.73.

The average compressibility¹² at 20° C. between 100 and 500 megabars¹³ is 2.4×10^{-6} .

The linear thermal expansion¹⁴ between the temperatures -190° C. and 17° C. is given by the expression

¹ Cohen, *J. Soc. Chem. Ind.*, 1929, 48, 64; Cohen and Ringer, *Zeitsch. physikal. Chem.*, 1904, 47, 1; Cohen, Collins and Strengers, *ibid.*, 1905, 50, 291; Cohen and Strengers, *ibid.*, 1905, 52, 129.

² See also Friend, "A Text-Book of Physical Chemistry" (Griffin, 1932), Vol. I, p. 179.

³ See p. 25.

⁴ Cohen and van den Bosch, *Proc. K. Wetensch. Amsterdam*, 1914, 17, 645; *Zeitsch. physikal. Chem.*, 1915, 89, 757; Jánecko, *ibid.*, 1915, 90, 337.

⁵ Schulze and Graf, *Metallwirtschaft*, 1933, 12, 19; Schulze, *Zeitsch. physikal. Chem.*, 1933, 165 A, 188.

⁶ Laspeyres, *Zeitsch. geol. Gesell.*, 1875, 27, 574; Kahlbaum, *Zeitsch. anorg. Chem.*, 1902, 29, 292.

⁷ James and Tunstall, *Phil. Mag.*, 1920, [6], 40, 233; Ogg, *Phil. Mag.*, 1921, [6], 42, 163; Solomon and Morris Jones, *Phil. Mag.*, 1930, [7], 10, 470; Neuburger, *Zeitsch. Krist.*, 1931, 80, 103.

⁸ Hirata, *Elec. Review (Japan)*, 1928, 16, 651.

⁹ Carpenter and Tamura, *Bull. Inst. Mining Met.*, 1928, 282, 1.

¹⁰ *International Critical Tables*, 1926, 1, 102. See also Cohen and van den Bosch, *Zeitsch. physikal. Chem.*, 1915, 89, 757; Lincke, *ibid.*, 1908, 56, 393; Guinchant and Chrétien, *Compt. rend.*, 1906, 142, 709; Kahlbaum, Roth and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 177.

¹¹ *International Critical Tables*, 1926, 1, 340.

¹² Richards and White, *J. Amer. Chem. Soc.*, 1928, 50, 3300.

¹³ 1 megabar = 10^6 dynes per sq. cm.

¹⁴ Valentiner and Wallot, *Verh. physikal. Ges. Berlin*, 1914, 16, 757; Grüneisen, *Ann. Physik*, 1910, 33, 33, 65. See also Fizeau, *Ann. Chim. Phys.*, 1866, [4], 8, 335; *Compt. rend.*, 1869, 68, 1125; Dorsey, *Phys. Review*, 1907, 25, 88; Lussano, *Nuovo Cimento*, 1910, 19, 182; Hidnert and Krider, *Phys. Review*, 1932, 42, 911.

$$l_t = l_0(1 + 0.0000102t)$$

and between the temperatures 17° C. and 100° C. by

$$l_t = l_0(1 + 0.00001088t)$$

The *cubical coefficient of expansion*¹ lies between 0.0000316 and 0.000033. The thermal expansion of single crystals has also been determined.²

The *hardness* of antimony on Mohs' scale lies between 3.0 and 3.5. The Brinell hardness number³ is 58.0, but higher values have been obtained. The *ultimate tensile strength*⁴ is 1.1 kilograms per square millimetre; *Young's modulus* is 7,950 kilograms per square millimetre, and the *modulus of elasticity in shear* 2,020 kilograms per square millimetre.

The *specific heat*⁵ is 0.05. Within the temperature range 412° C. to 460° C. the *heat capacity*⁶ is given by

$$H = 0.0534496 - 0.4522 \times 10^{-2}t + 0.7944 \times 10^{-5}t^2 \text{ gram-calories per gram}$$

The heat capacity at low temperatures has also been determined and is as follows :—⁷

Temperature, °C. .	+20.2	+ 4.6	- 8.5	- 20.1	- 32.4	- 46.0	- 58.5	- 70.4
Heat capacity .	6.073	6.043	5.940	5.923	5.943	5.893	5.878	5.834
(Gram-calories per gram-atom)								
Temperature, °C. .	-80.0	-91.1	-103.6	-133.3	-158.2	-170.9	-197.3	-207.0
Heat capacity .	5.789	5.726	5.691	5.431	5.224	4.700	4.337	3.917
(Gram-calories per gram-atom)								

From this the entropies have been calculated.

The *melting point*⁸ is 630.5° C., the metal being very susceptible to supercooling.⁹

¹ Matthiessen, *Pogg. Annalen*, 1838, 43, 390; Kopp, *Annalen*, 1852, 81, 1; *Pogg. Annalen*, 1852, 86, 156.

² Bridgman, *Proc. Nat. Acad. Sciences*, 1924, 10, 411; Braesco, *Compt. rend.*, 1920, 170, 103.

³ Edwards and Herbert, *J. Inst. Metals*, 1921, 25, 175; *Metal Industry*, London, 1921, 18, 221. See also Sauerwald, *Zeitsch. Metallkunde*, 1924, 16, 315.

⁴ Bridgman, *Phys. Review*, 1917, 9, 138.

⁵ Awberry and Griffiths, *Proc. Phys. Soc.*, 1926, 38, 378. See also Dulong and Petit, *Ann. Chim. Phys.*, 1818, [2], 7, 146; Regnault, *ibid.*, 1840, [2], 73, 42; Kopp, *ibid.*, 1852, [3], 34, 339; *Annalen*, 1852, 81, 34; Naccari, *Gazzetta*, 1888, 18, 13; Laborde, *Compt. rend.*, 1896, 123, 227; Behn, *Ann. Physik*, 1900, 1, 257; Kahlbaum, Roth and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 177; Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, 70, 414; Schimpff, *ibid.*, 1910, 71, 257; Dewar, *Proc. Roy. Soc.*, 1913, A 89, 158; Schübel, *Zeitsch. anorg. Chem.*, 1914, 87, 81; Ewald, *Ann. Physik*, 1914, 44, 1213; Wust, Meuthen and Durrer, "Die Temperatur Warmenhaltskurven der technisch wichtigen Metalle," Berlin, 1918; Günther, *Ann. Physik*, 1920, [4], 63, 476; Simon and Ruhemann, *Zeitsch. physikal. Chem.*, 1927, 129, 321.

⁶ Bottema and Jaeger, *Proc. Acad. Sci. Amsterdam*, 1932, 35, 916.

⁷ Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2712. See also Kelley, *Bur. Mines Bull.*, 1932, p. 350.

⁸ Awberry and Griffiths, *loc. cit.* See also Heycock and Neville, *J. Chem. Soc.*, 1895, 67, 186; Gautier, *Compt. rend.*, 1896, 123, 112; Callendar, *Phil. Mag.*, 1899, [5], 48, 519; Holborn and Day, *Ann. Physik*, 1900, [4], 2, 534; van Aubel, *Compt. rend.*, 1901, 132, 1266; Fay and Ashley, *Amer. Chem. J.*, 1902, 27, 95; Krafft, *Ber.*, 1903, 36, 1712; Chrétien, *Compt. rend.*, 1906, 142, 1340; Laschtschenko, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 311.

⁹ Reinders, *Zeitsch. anorg. Chem.*, 1900, 25, 119.

When molten antimony is cooled its colour diminishes in brightness in a normal manner until the solidification point is reached; at this point a sudden increase in brightness occurs, accompanied by an increase in temperature. As this phenomenon occurs in an atmosphere of hydrogen as well as in a vacuum, it cannot be ascribed to oxidation, and is considered to be an instance of crystal luminescence.¹ The ratio of the spontaneous crystallising power to the linear velocity of crystallisation² increases with the velocity of cooling in the temperature range between 600° C. and -70° C. As the spontaneous crystallising power diminishes at low temperatures, it may be possible to obtain amorphous antimony by very drastic supercooling.

The latent heat of fusion is 38.84 calories per gram.³

The values obtained by earlier workers for the volume change on solidification are confusing, the general conclusion being that the change is very small, antimony probably resembling bismuth in expanding on solidification. Toepler⁴ concluded that there was a shrinkage on solidification to the extent of 1.4 per cent. or 0.0022 c.c. per gram. A more recent investigation, however, has revealed an expansion on solidification of 0.95 per cent., a result which appears to have been confirmed.⁵

The density of molten antimony is shown in the following table, though different investigators have obtained slightly different results: ⁶

Temperature, °C.	640	700	800	970
Density	6.49	6.45	6.38	6.29

The variation of surface tension, σ , of molten antimony with temperature is as follows:

Temperature, °C.	640	675	700	800	974
σ (dynes per cm.)	348	350	350	348	342

From a consideration of these values it is deduced that antimony in the molten state is probably highly associated.⁷ The observed parachor⁸ varies from 76.8 to 83.9, the calculated value being 66.0.

The mean specific heat of the liquid⁹ is 0.16.

The coefficient of viscosity,¹⁰ measured in grams per cm. per sec., is as follows:

Temperature, °C.	702	801	902	1002
Viscosity	0.01804	0.01113	0.01010	0.00905

¹ Karrer, *Phys. Review*, 1922, 19, 437.

² Bekier, *Zeitsch. anorg. Chem.*, 1912, 78, 178.

³ *International Critical Tables*, 1927, 2, 458. See also Awberry and Griffiths, *loc. cit.*; Laschtschenko, *loc. cit.*

⁴ Toepler, *Ann. Phys. Chem.*, 1894, [2], 53, 343.

⁵ Matsuyama, *Science Rep. Tohoku Imp. Univ.*, 1928, 17, 1. See also Parlitiz, *Sitzungsber. Naturforsch. Ges. Univ. Tartu*, 1929, 35, 121; Broniewski, *Inst. Intern. Phys. Solvay*, 4th Conseil, 1924, 1927, 185.

⁶ Quincke, *Pogg. Annalen*, 1868, 135, 621; Guinchant and Chrétien, *Compt. rend.*, 1906, 142, 709; Pascal and Jouriaux, *Compt. rend.*, 1914, 158, 414; Bornemann and Sauerwald, *Zeitsch. Metallkunde*, 1922, 14, 254; Bircumshaw, *Phil. Mag.*, 1927, [7], 3, 1290; Matsuyama, *Science Rep. Tohoku Imp. Univ.*, 1929, 18, 737.

⁷ Bircumshaw, *Phil. Mag.*, 1927, [7], 3, 1286. See also Smith, *J. Inst. Metals*, 1914, 12, 168; Drath and Sauerwald, *Zeitsch. anorg. Chem.*, 1927, 162, 301; Antonoff, *Nature*, 1928, 121, 93.

⁸ Sugden and Wilkins, *J. Chem. Soc.*, 1929, 132, 1291.

⁹ Awberry and Griffiths, *loc. cit.*

¹⁰ Bienias and Sauerwald, *Zeitsch. anorg. Chem.*, 1927, 161, 51.

The *boiling point* under atmospheric pressure¹ is $1635^{\circ}\text{C.} \pm 8^{\circ}\text{C.}$ This value is much higher than that given by previous investigators, as will be seen from the following data for the vapour pressure of antimony:²

Temperature, $^{\circ}\text{C.}$	1075	1135	1175	1225	1265	1325	1380
Pressure (mm.)	54	107	206	302	398	745	760

Under reduced pressure³ volatilisation is said to take place at temperatures as low as 292°C.

The *vapour density* of antimony indicates that at high temperatures the vapour is probably monatomic,⁴ association taking place at lower temperatures.⁵

The *thermal conductivity* of solid antimony lies between 0.038 and 0.050 gram-calories per cm. per sec.; the probable mean value⁶ is 0.044. The effects of pressure⁷ and of temperature⁸ upon the thermal conductivity have been investigated.

The *electrical resistance* at various temperatures is shown in the following table:⁹

Temperature, $^{\circ}\text{C.}$	Resistance (ohm-cm.).	R/R_0 .
15	8.28×10^{-4}	1.08
0	7.66×10^{-4}	1.00
-191	2.08×10^{-4}	0.265
-242.4	0.696×10^{-4}	0.0909
-268.8	0.580×10^{-4}	0.0760

The influence of strong magnetic fields¹⁰ upon the electrical resistance has also been investigated; while the electrical resistance of molten antimony at the melting point is 115.0×10^{-6} ohm-cm.¹¹ Both the

¹ Leitgeb, *Zeitsch. anorg. Chem.*, 1931, 202, 305.

² Ruff and Bergdahl, *Zeitsch. anorg. Chem.*, 1919, 106, 76. See also Carnelley and Williams, *J. Chem. Soc.*, 1879, 35, 563; Meyer and Mensching, *Annalen*, 1887, 240, 321; *Ber.*, 1887, 20, 500, 1833; Meyer and Biltz, *Ber.*, 1889, 22, 725; *Zeitsch. physikal. Chem.*, 1889, 4, 249; Greenwood, *Proc. Roy. Soc.*, 1909, 82, 396; *Zeitsch. Elektrochem.*, 1912, 18, 319; van Liempt, *Zeitsch. anorg. Chem.*, 1920, 114, 105; 1920, 111, 280.

³ Krafft and Bergfeld, *Ber.*, 1905, 38, 258; Krafft, *ibid.*, 1903, 36, 1704; Schuller, *Wied. Annalen*, 1883, 18, 321; Demarçay, *Compt. rend.*, 1882, 95, 183. See also Zenghelis, *Zeitsch. physikal. Chem.*, 1906, 57, 90.

⁴ von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 56, 320.

⁵ Meyer and Biltz, *loc. cit.* See also Ruff and Mugdan, *Zeitsch. anorg. Chem.*, 1921, 117, 147; Ruff and Bergdahl, *loc. cit.*

⁶ *International Critical Tables*, 1929, 5, 220. See also Eucken and Gehlhoff, *Ber. deut. physikal. Ges.*, 1912, 14, 169; Gehlhoff and Neumeier, *ibid.*, 1913, 15, 876; Eucken and Neumann, *Zeitsch. physikal. Chem.*, 1924, 111, 431.

⁷ Bridgman, *Proc. Amer. Acad. Arts and Sciences*, 1922, 57, 77; 1923, 59, 119.

⁸ Lorentz, *Pogg. Annalen*, 1872, 147, 429; *Wied. Annalen*, 1881, 13, 422, 582; Janettaz, *Ann. Chm. Phys.*, 1873, [4], 29, 38; Matthiessen, *ibid.*, 1858, [3], 54, 255; Gehlhoff and Neumeier, *Ber. deut. physikal. Ges.*, 1913, 15, 1069.

⁹ McLennan, Niven and Wilhelm, *Phil. Mag.*, 1928, [7], 6, 666. See also Meissner, *Zeitsch. Ges. Kälte-Ind.*, 1929, 36, 62; Meissner and Voigt, *Ann. Physik*, 1930, [5], 7, 892.

¹⁰ Kapitza, *Proc. Roy. Soc.*, 1929, A 123, 292.

¹¹ Matsuyama, *Kinsoku no Kenko*, 1926, [4], 3, 254; *Trans. Amer. Soc. Steel Treatment*, 1926, 10, 318. See also Matthiessen, *loc. cit.*; Erhard, *Wied. Annalen*, 1881, 14, 504; Gehlhoff and Neumeier, *Ber. deut. physikal. Ges.*, 1913, 15, 876; Northrup and Suydam, *J. Franklin Inst.*, 1913, 175, 153; Bridgman, *Proc. Amer. Acad. Arts and Sciences*, 1933, 68, 95; Allen, *Phys. Review*, 1933, 43, 569.

temperature coefficient and the pressure coefficient ¹ have been determined.

For an *antimony-platinum couple*, if the cold junction is maintained at 0° C., the *thermo-electromotive force* in microvolts may be calculated for any temperature between 0° C. and 630° C. from the equation : ²

$$_{\text{Sb}}E_{\text{Pt}} = 46 \cdot 24t + 0 \cdot 0313t^2 - 0 \cdot 0000477t^3$$

and the *thermo-electric power*, in microvolts per degree centigrade, from the equation :

$$_{\text{Sb}}Q_{\text{Pt}} = 46 \cdot 24 + 0 \cdot 0636t - 0 \cdot 00001433t^2$$

The *magnetic susceptibility*, using a field lying between 1029 and 13,680 gauss, is $-0 \cdot 8138 \times 10^{-6}$. This value appears to be independent of the field strength.³ For a single crystal the mean magnetic susceptibility ⁴ is $-0 \cdot 80 \times 10^{-6}$, the susceptibility depending upon the position of the crystallographic axis with respect to the direction in which the susceptibility is measured. There is little variation in the susceptibility between room temperature and that of liquid air. The magnetic anisotropy is ascribed to the unequal valency group in this element.⁵ The influence of particle size upon the diamagnetic susceptibility of antimony has been examined. According to some investigators ⁶ the diamagnetic susceptibility falls as the size of particle decreases, tending to become constant at a diameter less than $0 \cdot 5\mu$. It has also been stated, however, that the size of particle is practically without effect.⁷

The *Hall effect* ⁸ at 20° C. in a magnetic field lying between 4 and 16 kilogauss is $+19 \cdot 2 \times 10^{-9}$ volt-cm. per ampere-gauss. The variation of Hall effect with temperature,⁹ and with variation of the magnetic field,¹⁰ has been investigated. The *Corbino effect*,¹¹ *Ettingshausen effect*,¹² *Nernst effect*¹³ and *Righi-Leduc effect*¹⁴ have also been examined.

The *refractive index* ¹⁵ varies from 3.04 to 3.17, according to wavelength, the corresponding absorption coefficients varying from 1.63 to 1.56.

Explosive, Amorphous or β -Antimony is usually obtained by the electrolysis of solutions of antimony trichloride. It was first

¹ Bridgman, *Proc. Amer. Acad. Arts and Sciences*, 1917, 52, 573; 1922, 57, 48.

² *International Critical Tables*, 1929, 6, 214; Pélabon, *Ann. physique*, 1920, 13, 169; *Compt. rend.*, 1923, 176, 1309.

³ Isnardi and Gans, *Ann. Physik*, 1920, [4], 61, 585; Owen, *ibid.*, 1912, [4], 37, 657; Honda, *Ann. Physik*, 1910, [4], 32, 1027.

⁴ McLennan and Cohen, *Trans. Roy. Soc. Can.*, 1929, Section III, [3], 23, 159. See also de Haas and van Alphen, *Proc. Acad. Sci. Amsterdam*, 1933, 36, 263.

⁵ Vaidyanathan, *Indian J. Physics*, 1930, 5, 559.

⁶ Rao, *Indian J. Physics*, 1931, 6, 241; *Nature*, 1931, 128, 153; Vaidyanathan, *loc. cit.*; *Nature*, 1930, 125, 672.

⁷ Verma and Mathur, *J. Indian Chem. Soc.*, 1933, 10, 321.

⁸ Ettingshausen and Nernst, *Sitzungsber. K. Akad. Wiss. Wien*, 1886, 94 II, 560; Barlow, *Ann. Physik*, 1903, 12, 897; Zahn, *ibid.*, 1904, 14, 886; Alterthum, *ibid.*, 1912, 39, 933.

⁹ Alterthum, *loc. cit.*; Barlow, *loc. cit.*

¹⁰ Barlow, *loc. cit.*; Cantone and Bossa, *Mem. accad. Italia*, Fis. 2, 1930, No. 1.

¹¹ Adams and Chapman, *Phil. Mag.*, 1914, [6], 28, 692; Chapman, *ibid.*, 1916, [6], 32, 303.

¹² Zahn, *loc. cit.*; Barlow, *loc. cit.*

¹³ Zahn, *loc. cit.*; Barlow, *loc. cit.*; Nernst, *Wied. Annalen*, 1887, 31, 760.

¹⁴ Zahn, *loc. cit.*; Barlow, *loc. cit.*; Alpheus W. Smith and Alva W. Smith, *Phys. Review*, 1915, [2], 5, 35.

¹⁵ Drude, *Wied. Annalen*, 1890, 39, 481.

prepared by Gore¹ in October 1854 from solutions of antimony trichloride, tribromide and triiodide. The product obtained in each case was different, and in each case was contaminated with the corresponding halide, that from the solution of antimony trichloride containing about 6 per cent. of halide, and that from the solution of antimony triiodide about 22.2 per cent. Two specimens obtained from the electrolysis of antimony trichloride gave the following analysis :

Sb	93.36	93.51
SbCl ₃	5.98	6.08
HCl	0.46	0.21
					<hr/>	<hr/>
					99.80	99.75

Gore concluded that this variety of antimony was either capable of forming an unstable compound of indefinite composition with antimony halides, or that it was an amorphous variety in which the halide was mechanically entangled.

Both crystalline and amorphous antimony may be obtained by electrodeposition from solutions of antimony trichloride in hydrochloric acid, the nature of the deposit depending upon the temperature, concentration and current density,² increase in temperature and decrease in current density favouring the formation of the crystalline modification. Cathodes of platinum, copper, manganin, graphite, zinc and mercury have been employed.³ X-ray examination of the deposit obtained from solutions of antimony trichloride in glacial acetic acid, using a copper cathode, indicates that the nature of the deposit is not affected by a change in current density from 0.1 to 0.7 ampere per square centimetre ; that for a given concentration amorphous antimony is deposited at a higher temperature than from aqueous solutions (particularly at lower concentration), while at a given temperature amorphous antimony is deposited at lower concentrations than from aqueous solutions.⁴ Amorphous antimony is deposited from solutions in glacial acetic acid containing 10 grams SbCl₃ in 100 grams solution below 40° C., and from solutions containing 50 grams SbCl₃ in 100 grams solution below 55° C. Within this range a mixed deposit is obtained.

Thin layers of antimony deposited on cellulose nitrate films show, from electron diffraction patterns, an amorphous structure if the deposit is not too thick, while thick deposits show only a crystalline structure. With very thin layers the amorphous structure persists indefinitely, while with deposits of medium thickness crystalline spots appear after a time and gradually spread throughout the deposit.⁵

A black, amorphous modification of antimony, probably identical with that described by Cohen, has been prepared by the action of oxygen or air on liquid antimony trihydride cooled to about -40° C. ; and also by the rapid cooling of antimony vapour.⁶ A similar product has been obtained by the reduction of antimony compounds in the presence of

¹ Gore, *Phil. Mag.*, 1855, [4], 9, 73; *Phil. Trans.*, 1858, 148, 185, 797; 1862, 152, 323; *J. Chem. Soc.*, 1863, 16, 365.

² Kersten, *Physics*, 1932, 2, 276; Cohen and Coffin, *Zeitsch. physikal. Chem.*, 1930, 149 A, 417; Böhm, *Zeitsch. anorg. Chem.*, 1925, 149, 217.

³ von Steinwehr and Schulze, *Zeitsch. Physik*, 1930, 63, 815.

⁴ Stillwell and Audrieth, *J. Amer. Chem. Soc.*, 1932, 54, 472.

⁵ Prins, *Nature*, 1933, 131, 760.

⁶ Stock and Siebert, *Ber.*, 1905, 38, 3837.

antimony trichloride.¹ In the absence of the trichloride, however, only the crystalline modification is obtained.

By heating antimony in a stream of nitrogen a substance resembling amorphous antimony has been obtained;² it is stated, however, to be a mixture of antimony with antimony trioxide,³ and was not obtained when pure antimony and pure nitrogen were used.

A vitreous amorphous form of antimony has also been formed⁴ by the rapid quenching of small drops of antimony which has been fused with antimony triselenide. The presence of antimony triselenide retards the crystallisation of antimony considerably. These amorphous

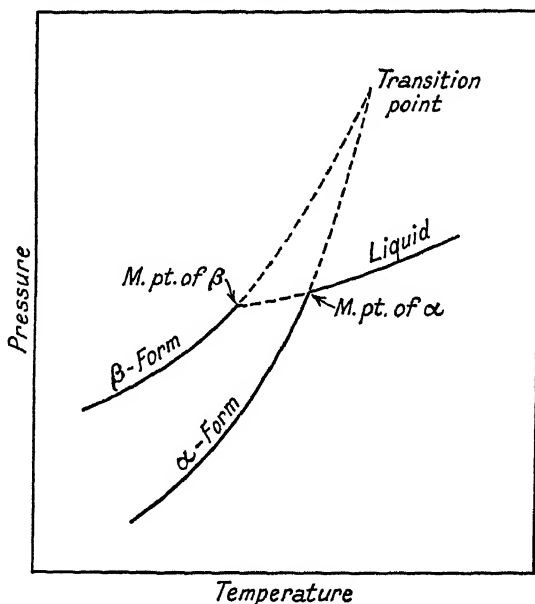


FIG. 1.—Vapour Pressure Curves of Antimony.

pellets are moderately stable even when heated to 500° C., but crystallise much more rapidly at 520° C.

Amorphous or β -antimony is metastable at all temperatures below the melting point. The transformation to the stable rhombohedral or α -form takes place very slowly at ordinary temperatures, particularly in the absence of any external stimulus. If the β -allotrope is scratched, however, the transformation takes place much more rapidly, and may even approach explosive violence. The system is probably monotropic; the conditions of equilibrium are represented diagrammatically⁵ in fig. 1. It will be seen that the vapour pressure of the β -allotrope is always higher than that of the more stable α -form, and that the two vapour pressure curves intersect at a point (the "transition point") above the melting points of both allotropes.

¹ Levi and Ghiron, *Atti R. Accad. Lincei*, 1933, [6], 17, 565.

² Hérard, *Compt. rend.*, 1888, 107, 420.

³ Cohen and Olie, *Zeitsch. physikal. Chem.*, 1908, 61, 588.

⁴ Tammann and Muller, *Zeitsch. anorg. Chem.*, 1934, 221, 109.

⁵ Cohen, *J. Soc. Chem. Ind.*, 1929, 48, 162; Friend, "A Text-Book of Physical Chemistry" (Griffin, 1932), Vol. I, p. 179.

Amorphous antimony obtained by electrolysis is always contaminated by antimony halides, and it has been shown that the halides are not held mechanically; ¹ it is assumed that these preparations are solid solutions of antimony halide in the metastable β -allotrope, ² and on this assumption it is possible to formulate an explanation of the explosive nature of the transformation from β to α . When amorphous antimony is scratched, the heat developed by the scratch is sufficient to accelerate appreciably the rate of transformation. As the transformation itself is exothermic (see below), the surrounding material becomes heated, and thus the transformation progresses almost instantaneously throughout the mass. Allowing for heat losses by radiation, etc., the rise in temperature is sufficient to volatilise the contaminating antimony halide, and this rapid volatilisation is responsible for the explosive effect. It should be stated, however, that a transition temperature of 96° to 100° C. for the transformation from β - to α -antimony has recently been reported. ³

Photomicrographs of explosive antimony (deposited electrolytically) have been examined before and after the "explosion." (The "explosion" was effected by a spark from an induction coil or from a Leyden jar, or by touching the film with a hot needle). The polished surface before the explosion resembles that of any other soft bright metal. After the explosion, a very large number of fine lines is, however, developed, parallel in that part of the film remote from the origin of the explosion, but arranged in concentric circles around that origin. These lines apparently are not a surface effect. ⁴

The *heat of transformation* is 20 gram-calories per gram. ⁵

The *heat capacity* ⁶ between 150° C. and 411° C. is given by

$$H = 0.0535656 - 0.46635 \times 10^{-4}t + 0.15497 \times 10^{-6}t^2 \text{ gram-calories per gram.}$$

The *specific electrical resistance* ⁷ is 50,000 to 90,000 times greater than that of rhombohedral antimony.

Yellow Antimony, an unstable allotrope, has been prepared by the action of oxygen on antimony trihydride at -90° C., and by the action of antimony trihydride on chlorine dissolved in ethane at -100° C. in red light. ⁸ It has only been obtained in very minute quantities, reverting (above -90° C.) to the black (probably amorphous) modification. It is believed to be isomorphous with yellow phosphorus and yellow arsenic.

By condensing the vapour of antimony obtained by cathode spluttering, the metal can be obtained in a form which has an extremely high electrical resistance. ⁹ In this condition the characteristic X-ray patterns are no longer obtained, thus suggesting that the metal is now amorphous. By heating to 178° C. the normal form of the metal is again obtained.

Spectrum.—Antimony compounds impart no characteristic coloration to the Bunsen flame. The wavelengths of the principal lines of the *arc spectrum*, measured in Angstrom units [$1 \text{ \AA} = 10^{-8} \text{ cm.}$], are given

¹ Cohen and Ringer, *Zeitsch. physikal. Chem.*, 1904, 47, 1.

² Cohen and Strengers, *ibid.*, 1905, 52, 129.

³ von Steinwehr and Schulze, *loc. cit.* See also Levi and Ghiron, *loc. cit.*; Schulze and Graf, *Metallwirtschaft*, 1933, 12, 19; Schulze, *Zeitsch. physikal. Chem.*, 1933, 165, 188.

⁴ Coffin and Johnston, *Proc. Roy. Soc.*, 1934, 146 A, 564.

⁵ Cohen and Strengers, *loc. cit.* See, however, von Steinwehr and Schulze, *loc. cit.*

⁶ Bottema and Jaeger, *Proc. Acad. Sci. Amsterdam*, 1932, 35, 916.

⁷ von Steinwehr and Schulze, *loc. cit.*

⁸ Stock and Siebert, *Ber.*, 1905, 38, 3837.

⁹ Kramer, *Ann. Physik*, 1934, [5], 19, 37.

below. The numbers in parenthesis indicate the relative intensities of the lines, the lowest numbers indicating the weakest intensities. Wave-lengths marked (a) are those of lines emitted by the neutral atom, those marked R are of lines that are easily reversed.¹

11864 (4), 11268 (4), 10840 (5), 10743 (5), 10678 (10), 10587 (5), 10263 (4), 10080 (4), 7924.6 (6), 7844.4 (4), 6806.3 (6), 6778.4 (6), 6129.9 (6), 6079.6 (6), 6005.0 (6), 5780.4 (4), 5632.0 (4), 4033.5 (6 a), 3722.8 (8 a), 3637.8 (9 a), 3383.2 (5 a), 3267.48 (8 a R), 3232.52 (8 a R), 3029.8 (8 a R), 2877.920 (10 a R), 2851.1 (4), 2769.95 (10 a R), 2727.22 (5 R), 2682.77 (4 R), 2670.67 (5 a R), 2598.076 (10 a R), 2528.53 (6 a R), 2373.7 (4 R), 2311.5 (6 a R), 2306.5 (5 R), 2179.25 (4 R), 2175.88 (5 a R), 2068.38 (4 a R).

The principal lines of the *spark spectrum* are :

5639.7 (5), 4693.0 (10), 4591.8 (5), 4352.2 (10), 4265.0 (10), 4195.1 (8), 4033.5 (4 a), 3722.8 (5 a), 3637.8 (6 a), 3504.5 (10 a), 3498.5 (10), 3473.9 (10), 3267.5 (10 a), 3241.2 (10), 3232.5 (10 a), 3040.7 (10), 3029.8 (10 a), 2918.3 (5), 2877.920 (10 a R), 2851.1 (4), 2790.4 (10), 2769.95 (10 a R), 2727.22 (8), 2718.90 (10), 2682.77 (5), 2670.67 (5 a), 2652.60 (8), 2612.32 (8), 2598.076 (10 a R), 2590.29 (10), 2528.54 (10 a R), 2478.34 (6), 2445.55 (6 a), 2383.64 (4), 2311.5 (10 a R), 2306.5 (4), 2054.0 (6), 2039.7 (5), 2023.9 (4), 1926.6 (5), 1870.6 (10), 1867 (8), 1810 (5), 1783 (10), 1762 (10), 1731 (5), 1725 (6), 1712 (6), 1585 (8), 1566.3 (8), 1514 (10), 1438 (10), 1307 (10), 1225 (10), 1211 (10), 1205 (10), 1193 (10), 1171 (10), 1168 (10), 1162 (10), 1048 (10), 1042 (10), 1012 (10), 981 (10), 976 (10), 861 (6), 805 (5).

The most persistent lines emitted by the neutral atom, together with the combinations of spectral terms (energy states) from which they arise are : ² 2068.38(⁴S₂ - ⁴P₃), 2175.88(⁴S₂ - ⁴P₂), 2311.50(⁴S₂ - ⁴P₁), 2528.53(²D₃ - ²P₂), 2598.08(²D₂ - ²P₁), 3232.52(²P'₂ - ²P₂), 3267.48(²P'₁ - ²P₁).

The *absorption spectrum* of antimony vapour shows a banded structure extending from λ 2305 to λ 2250 Å. with a constant interval of nearly 15 Å. At higher temperatures another banded structure occurs in the region λ 2830 to λ 3000 Å. Fine lines have also been observed at λ 2312 and λ 2306 Å. and at higher temperatures at λ 2770 Å., but subsequent investigation failed to reveal these lines.³

From a study of the absorption spectrum⁴ it has been suggested that three types of diatomic molecules can exist in the vapour of antimony and that they occur in the proportions

$$(\text{Sb}^{121})_2 : \text{Sb}^{121}.\text{Sb}^{123} : (\text{Sb}^{123})_2 = 5 : 8 : 3$$

In the accompanying bibliography references are given to the more important researches dealing with the *arc spectrum*,⁵ and deductions

¹ *International Critical Tables*, 1929, 5, 312. A bibliography is included.

² *International Critical Tables*, 1929, 5, 324.

³ Frayne and Smith, *Phil. Mag.*, 1926, [7], i, 732. See also Narayan, *ibid.*, 1925, [6], 50, 645; Dobbie and Fox, *Proc. Roy. Soc.*, 1920, 98 A, 147; Charola, *Physikal. Zeitsch.*, 1930, 31, 457; Ruark, Mohler, Foote and Chenault, *U.S. Bureau of Standards, Science Papers*, 1924, 19, No. 490, 463; Nakamura and Shidei, *Japan J. Physics*, 1935, 10, 11.

⁴ S. M. Naudé, *Phys. Review*, 1934, 45, 280.

⁵ Kretzer, *Zeitsch. wiss. Photochem.*, 1910, 8, 45; Green and Loring, *Phys. Review*, 1928, 31, 707; Charola, *loc. cit.*; *Univ. La Plata, Estudios Ciencias*, 1929, 89, 205; Malurkar, *Proc. Camb. Phil. Soc.*, 1928, 24, 85; McLennan and McLay, *Trans. Roy. Soc. Canada*, 1928, [3], 21, III, 63; Ruark, Mohler, Foote and Chenault, *loc. cit.*; Pina de Rubies and Bagues, *Zeitsch. anorg. Chem.*, 1933, 215, 205; Kraemer, *Zeitsch. anal. Chem.*, 1934, 97, 89.

from it regarding *sub-atomic structure*,¹ the *spark spectrum*,² the *flame spectrum*,³ the *ultra-violet spectrum*,⁴ *series spectra*,⁵ the *ultimate rays*,⁶ the *Zeemann effect*,⁷ and the *critical potential*, *resonance potential* and *thermionic discharge spectra*.⁸

From the spark spectra of antimony in various degrees of ionisation it is calculated that the *ionisation potential* for singly ionised antimony⁹ is 18 volts (or 18.8 volts), and that for doubly ionised antimony¹⁰ 24.7 volts.¹¹

By illuminating the vapour of diatomic antimony by a mercury arc of high luminosity, a rather strong *fluorescence* has been obtained, excited by four mercury lines and possibly by two others.¹²

The wavelengths of the most persistent lines in the spark spectrum of solutions of antimony chloride, together with the dilution at which the lines persist,¹³ are as follows :

1 per cent. to 0.1 per cent. Sb+++	0.1 per cent. to 0.01 per cent. Sb+++	0.01 per cent. to 0.001 per cent. Sb+++
3739.95
3597.51
3504.51
3337.15
3267.53
3232.54
3029.86	3029.86	..
2877.92	2877.92	2877.92
2790.89	2790.89	..
2598.08	2598.08	2598.08
2528.54	2528.54	..
2311.48

¹ McLennan and McLay, *loc. cit.*; Green and Lang, *Proc. Nat. Acad. Science*, 1928, 14, 706.

² Kretzer, *loc. cit.*; Dhavale, *Nature*, 1930, 126, 97; Lang, *Phys. Review*, 1930, [2], 35, 445; Campetti, *Nuovo Cim.*, 1928, 5, 291; Soullilon, *Compt. rend.*, 1929, 188, 1103; Pattabhiramiah and Rao, *Indian J. Physics*, 1929, 3, 437. ³ Kretzer, *loc. cit.*

⁴ Bloch, *Compt. rend.*, 1924, 178, 472; 1920, 171, 709.

⁵ Lang, *Proc. Nat. Acad. Science*, 1927, 13, 341; van Lohnigen, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 31.

⁶ de Gramont, *Compt. rend.*, 1908, 146, 1260.

⁷ van der Harst, *Arch. Néerland.*, 1925, [3 A], 9, 1; *Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 300; Purvis, *Proc. Camb. Phil. Soc.*, 1907, 14, 217; Löwenthal, *Zeitsch. Physik*, 1929, 57, 822; Green and Loring, *loc. cit.*

⁸ Ruark, Mohler, Foote and Chenault, *loc. cit.*; Siksna, *Compt. rend.*, 1933, 196, 1986. For further reference to the spectra of antimony, see Gibbs, Vieweg and Gartlein, *Phys. Review*, 1929, 34, 406; Gibbs and Vieweg, *loc. cit.*, p. 400; Negresco, *J. Chim. phys.*, 1928, 25, 363; Green and Lang, *Nature*, 1928, 122, 241; Zumstein, *Phys. Review*, 1927, 29, 209.

⁹ Lang and Vestrine, *Phys. Review*, 1932, 42, 233; Dhavale, *Proc. Roy. Soc.*, 1931, A 131, 109. ¹⁰ Lang, *Phys. Review*, 1930, 35, 445.

¹¹ See also Badami, *Proc. Phys. Soc. London*, 1931, 43, 538; Lang, *Phys. Review*, 1932, 39, 538; Ricardi, *Atti R. Accad. Lincei*, 1927, [6], 6, 428.

¹² Genard, *Nature*, 1933, 131, 132; *Phys. Review*, 1933, 44, 468. See also Siksna, *Compt. rend.*, 1933, 196, 1986.

¹³ Baly, "Spectroscopy" (Longmans, 1927), Vol. II, p. 144.

The *X-ray spectrum* has also been examined, the lines in the K series ¹ and the L series ² having been recorded.

Single crystals of antimony have been prepared, the methods adopted being, in general, similar to those employed for bismuth (see page 131). Among the properties of such single crystals that have been investigated are the *mechanical properties*,³ the *electrical resistance*,⁴ the *thermo-electric properties*,⁵ and the *magnetic susceptibility*.⁶

Chemical Properties of Antimony.

Antimony does not combine directly with hydrogen, and can be volatilised by heating in a stream of that gas.⁷ Antimony compounds are reduced by nascent hydrogen in acid (but not in alkaline) solution forming antimony trihydride or stibine. Metallic antimony is precipitated from solutions by hydrogen at high temperature and pressure.⁸ With solutions of antimony trichloride of concentrations up to 50 per cent., and hydrogen at a pressure up to 150 atmospheres, the quantity of precipitated material is proportional to the pressure. The reaction is of the first order with pressures between 15 and 150 atmospheres and concentrations less than normal. It is calculated that from a normal solution of antimony chloride at 20° C., with hydrogen at a pressure of 100 atmospheres, the precipitation of 1 per cent. of metal would require 160 years. Increase of hydrogen ion retards the precipitation of antimony.⁹ From the behaviour of antimony as a catalyst in the silent reaction between hydrogen and oxygen, the metal does not appear to absorb hydrogen.¹⁰

Antimony is not appreciably affected by exposure to dry air, but in the presence of light ¹¹ and moisture oxidation takes place.¹² It burns brilliantly even in very dry oxygen.¹³ It is oxidised to antimony pentoxide by ozone.¹⁴

It decomposes steam only at very high temperatures, hydrogen and

¹ Cork and Stephenson, *Phys. Review*, 1926, [2], 27, 530; Leide, *Compt. rend.*, 1925, 180, 1203; Ray, *Phil. Mag.*, 1924, [6], 48, 707; Walter, *Zeitsch. Physik*, 1924, 30, 357; Siegbahn, *Jarhb. Rad. Elektron.*, 1916, 13, 296.

² Hirata, *Proc. Roy. Soc.*, 1924, A 105, 40; Kellstrom, *Zeitsch. Physik*, 1927, 44, 269; Pokrowsky, *Zeitsch. Physik*, 1926, 35, 390; Ray, *loc. cit.*; Dauvillier, *Compt. rend.*, 1921, 173, 1458; Coster and Mulder, *Zeitsch. Physik*, 1926, 38, 264; Lindsay, *Compt. rend.*, 1922, 175, 150; Hjalmar, *Zeitsch. Physik*, 1920, 3, 362; Druyvesteyn, *Zeitsch. Physik*, 1927, 43, 707; Coster, *Phil. Mag.*, 1922, [6], 43, 1078. See also Chamberlain, *Nature*, 1924, 114, 500; *Phys. Review*, 1925, [2], 26, 525; Chamberlain and Lindsay, *Phys. Review*, 1927, [2], 30, 369; Blake and Duane, *Phys. Review*, 1917, [2], 10, 697; Jonsson, *Zeitsch. Physik*, 1926, 35, 387; *International Critical Tables*, 1929, 6, 35, 38.

³ Gough and Cox, *Proc. Roy. Soc.*, 1930, A 127, 431.

⁴ Bridgman, *Proc. Amer. Acad. Arts and Sciences*, 1929, 63, 351.

⁵ Bridgman, *loc. cit.*; *Proc. Nat. Acad. Sci.*, 1928, 14, 943.

⁶ McLennan and Cohen, *Trans. Roy. Soc. Canada*, 1929, [3], 23, III, 159; Nusbaum, *Phys. Review*, 1927, 29, 905.

⁷ Vandevelde, *Bull. Acad. Belg.*, 1895, [3], 30, 78; Böttger, *J. prakt. Chem.*, 1869, 107, 43.

⁸ Ipatiev and Nikolaiev, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 698.

⁹ Ipatiev, jun., *Ber.*, 1931, 64 B, 2725; Ipatiev and Tredorovitch, *J. Gen. Chem. Russ.*, 1931, 1, 729; *Ber.*, 1932, 65 B, 575.

¹⁰ Kröger, *Zeitsch. anorg. Chem.*, 1930, 194, 73.

¹¹ Schönbein, *Pogg. Annalen*, 1848, 75, 362; *J. prakt. Chem.*, 1855, 66, 272.

¹² Berzelius, *Schweigger's J.*, 1812, 6, 144; 1818, 22, 69; Proust, *Gehlen's Allg. J. Chem.*, 1805, 5, 543; *Gilbert's Annalen*, 1806, 25, 186.

¹³ Baker and Dixon, *Proc. Roy. Soc.*, 1888, 45, 1.

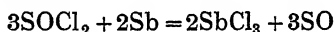
¹⁴ Schönbein, *loc. cit.*

antimony trioxide being formed; ¹ precipitated antimony reacts more readily.² Neutral hydrogen peroxide is without action, but in the presence of an alkali antimonates are formed.³

Antimony burns vigorously in fluorine; ⁴ it also combines directly with chlorine, bromine and iodine,⁵ with the first even when very dry.⁶ Hydrofluoric acid is without action, while hydrochloric acid attacks antimony only in the presence of air.⁷ The solvent action of hydrochloric acid is increased by the addition of a little nitric acid; ⁸ aqua regia converts the metal completely to antimony trichloride and antimony pentachloride. With nitrosyl chloride the compound $\text{SbCl}_5 \cdot \text{NOCl}$ is obtained.⁹

When antimony is fused with sulphur, combination takes place with the formation of antimony trisulphide. (It is doubtful whether either a higher or a lower sulphide is also formed.) The elements will also combine when heated together with water in a sealed tube to 200°C .; ¹⁰ and when a powdered mixture is subjected to high pressures.¹¹ Dry hydrogen sulphide attacks antimony at 360°C . and above, antimony trisulphide being formed; when the metal is heated moderately in a stream of sulphur dioxide, a mixture of antimony trioxide and antimony trisulphide is obtained.¹² Warm concentrated sulphuric acid attacks antimony forming antimony sulphate, but both dilute and cold acid are without action.

When antimony is heated with the vapour of thionyl chloride, the latter is decomposed with formation of antimony trichloride.¹³ Sulphur monoxide is also formed and it is suggested that the reaction proceeds according to the equation:



When antimony is heated in a stream of sulphuryl chloride (diluted with carbon dioxide) the metal is converted to the trichloride.¹⁴

Antimony does not combine with nitrogen. It is attacked by nitric acid with evolution of nitric oxide, the remaining products depending upon the concentration and temperature of the acid. The action takes place only slowly in the absence of nitrous acid.¹⁵ Antimony nitrate may be formed when cold, dilute acid is used; but more generally a

¹ Berzelius, *loc. cit.*; Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 362.

² Ditte, *Compt. rend.*, 1892, 115, 939. See also Thiele, *Annalen*, 1891, 263, 361; Ruff and Albert, *Ber.*, 1905, 38, 54; Cohen and Ringer, *Zeitsch. physikal. Chem.*, 1904, 47, 12.

³ Clark, *J. Chem. Soc.*, 1893, 63, 886.

⁴ Moissan, *Ann. Chim. Phys.*, 1887, [6], 12, 523; 1891, [6], 24, 247.

⁵ Floresco, *Bul. Fac. Stiinte Cernauti*, 1929, 3, 24; *Chem. Zentr.*, 1931, 1, 1586.

⁶ Cowper, *J. Chem. Soc.*, 1883, 43, 153.

⁷ Ditte and Metzner, *Compt. rend.*, 1893, 115, 936. See also Clasen, *J. prakt. Chem.*, 1864, 92, 477; von der Planitz, *Bull. Soc. chim.*, 1875, [2], 24, 69.

⁸ Cooke, *Proc. Amer. Acad. Arts and Sciences*, 1877, 13, 18; Robiquet, *Ann. Chim. Phys.*, 1817, [2], 4, 165.

⁹ Sudborough, *J. Chem. Soc.*, 1891, 59, 655.

¹⁰ Geitner, *Annalen*, 1864, 129, 359.

¹¹ Spring, *Ber.*, 1883, 16, 999.

¹² Uhl, *Ber.*, 1890, 23, 2154. See, however, Schiff, *Annalen*, 1861, 117, 95; Geitner, *loc. cit.*

¹³ Schenck and Platz, *Zeitsch. anorg. Chem.*, 1933, 215, 113.

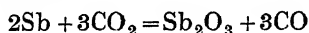
¹⁴ Danneel and Schlottmann, *Zeitsch. anorg. Chem.*, 1933, 212, 225. For the action of compounds containing chlorine and sulphur, see Heumann and Köchlin, *Ber.*, 1882, 15, 419, 1737; 1883, 16, 482, 1625.

¹⁵ Millon, *Ann. Chim. Phys.*, 1842, [3], 6, 101.

mixture of oxides of antimony is obtained.¹ The metal will not burn in the vapour of nitric acid.² It will dissolve in nitric acid to which has been added tartaric acid or certain other organic acids,³ and the solution remains clear on warming.⁴

Molten antimony combines readily with phosphorus. It reduces both phosphorus trioxide and phosphorus trisulphide when heated for a long time with those substances; it reacts quantitatively with phosphorus trichloride.⁵ When heated with phosphorus pentachloride, a mixture of antimony trichloride and phosphorus trichloride is obtained.⁶ The trichloride, trioxide and trisulphide of arsenic react similarly with antimony.

When antimony is heated in a current of carbon dioxide a reaction takes place, beginning at 830° C., and which, at 1100° C., may be represented by the equation ⁷



Antimony will react with the alkali metals forming antimonides.⁸ It is attacked by solutions of alkalis and of alkali salts.⁹ As has been stated above, antimony acts as a reducing agent under certain conditions; it will reduce the following salts, at least partially: ferric chloride,¹⁰ ferric sulphate, potassium ferricyanide, potassium nitrate,¹¹ and potassium permanganate (forming manganese dioxide).¹² The reduction of silver nitrate depends upon the concentration of the solution: from a 0.5*N* or 0.25*N* solution silver may be precipitated quantitatively, but with a weaker solution (0.05*N*) the reduction is incomplete, and a compound, $2\text{Sb}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$, is formed.¹³ Gold chloride is completely reduced by antimony.¹⁴ Antimony compounds are reduced to the metal by the action of Bettendorf's reagent (a mixture of stannous chloride and hydrochloric acid).¹⁵ Metallic antimony reacts with iron at the melting point of the former.¹⁶

The atomicity of antimony does not appear to be known with certainty. From a calculation of the heat of evaporation it has been deduced that antimony, between the boiling point and melting point, is monatomic,¹⁷ remaining in that condition when cooled to 357° C. At lower temperatures, polymerisation takes place. On the other hand, a

¹ Rose, *Pogg. Annalen*, 1841, 53, 161; Lefort, *J. Pharm. Chim.*, 1855, [3], 28, 93.

² Austen, *Chem. News*, 1889, 59, 208.

³ Streng, *Dingl. poly. J.*, 1859, 151, 389; Czerwek, *Zeitsch. anal. Chem.*, 1906, 45, 505.

⁴ For the action of other nitrogen compounds on antimony, see Curtius and Darapski, *J. prakt. Chem.*, 1900, [2], 61, 408; Sabatier and Senderens, *Bull. Soc. chim.*, 1892, [3], 7, 504; Daliotos, *Praktika*, 1931, 6, 92; *Chem. Zentr.*, 1931, ii, 1687.

⁵ Krafft and Neumann, *Ber.*, 1901, 34, 565; Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 425.

⁶ Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 12. For the action of phosphoric acid, see Portevin and Sanfourche, *Compt. rend.*, 1931, 192, 1563.

⁷ de Bacht, *Monatsh.*, 1916, 37, 119.

⁸ Lebeau, *Bull. Soc. chim.*, 1900, [3], 23, 250; *Compt. rend.*, 1900, 130, 502.

⁹ Ruff and Albert, *loc. cit.*

¹⁰ Attfield, *Zeitsch. anal. Chem.*, 1870, 9, 107.

¹¹ Böttger, *J. prakt. Chem.*, 1874, [2], 9, 195.

¹² Slater, *J. prakt. Chem.*, 1853, 60, 247.

¹³ Senderens, *Bull. Soc. chim.*, 1896, [3], 15, 218. See also Poleck and Thummel, *Ber.*, 1883, 16, 2446; Senderens, *Compt. rend.*, 1887, 104, 504.

¹⁴ Dexter, *Pogg. Annalen*, 1857, 100, 568.

¹⁵ Pagnello, *Boll. Chim. Farm.*, 1914, 53, 689.

¹⁶ Tammann and Scheerwächter, *Zeitsch. anorg. Chem.*, 1927, 167, 401.

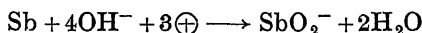
¹⁷ Jouriaux, *Bull. Soc. chim.*, 1924, [4], 35, 463.

theoretical calculation based upon van der Waal's equation indicated that the molecule of antimony may contain about twelve atoms.¹

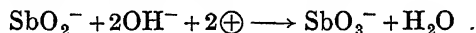
The normal electrode potential,² $\text{Sb}/\text{Sb}^{+++}$, is +0.244 volt measured on the hydrogen scale at summer temperature. In a 10N solution of potassium hydroxide at 20° C. the electrode potential³ is given by

$$E = -0.675 + \frac{0.058}{3} \log C_{\text{SbO}_2^-}$$

the process of solution being represented by



If the reaction proceeds according to the equation



then the potential is given by

$$E = -0.589 + \frac{0.058}{2} \log (C_{\text{SbO}_3^-}/C_{\text{SbO}_2^-})$$

Passivity of the antimony anode is not attained unless the current density exceeds 7.5 amperes per sq. dm.

The antimony electrode has recently received considerable attention.⁴ The electrode consists of a rod of metal connected by a copper wire to a calomel cell. The rod should be clean, and should dip into a solution containing suspended purified antimony trioxide, which should be stirred continuously. Cast antimony appears to be preferable to electrolytic metal.⁵ The value of E is given as⁶

$$E = +0.030 + 0.05915p\text{H}$$

The temperature coefficient is stated to be 0.0013 volt per degree in

¹ von Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 2.

² Jellinek and Gordon, *Zeitsch. physikal. Chem.*, 1924, 112, 207.

³ Grube and Schweigardt, *Zeitsch. Elektrochem.*, 1923, 29, 257.

⁴ Fenwick and Gilman, *J. Biol. Chem.*, 1929, 84, 605; Westenbrink and Peters, *Nederland. Tijdschr. Geneeskunde*, 1929, 73, I, 2973; Brinkman, *ibid.*, 1929, 73, II, 5000; Harrison and Vridhachalam, *Mem. Dept. Agr. India, Chem. Ser.*, 1929, 10, 157; Itano, *Ber. Ohara Inst. landw. Forsch. Japan*, 1929, [2], 4, 199, 273; Shukov and Gortikov, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 2055; *Zeitsch. Elektrochem.*, 1930, 35, 853; Vogel, *J. Soc. Chem. Ind.*, 1930, 49, 297 T; Hahn, *Zeitsch. angew. Chem.*, 1930, 43, 712; Lava and Hemedes, *Philippine Agr.*, 1928, 17, 337; Vlès and Vellinger, *Arch. phys. biol.*, 1927, 6, 38, 92; Brinkman and Buytendijk, *Biochem. Zeit.*, 1928, 199, 387; Brewer and Montillon, *Trans. Amer. Electrochem. Soc.*, 1909, 55; Buytendijk, *Arch. neerland. physiol.*, 1927, 12, 319; Roberts and Fenwick, *J. Amer. Chem. Soc.*, 1928, 50, 2125; Lindeman, *Meldinger Norges Landbruks*, 1926, 6, 302; Snyder, *Soil Science*, 1928, 26, 107; Kolthoff and Furman, "Potentiometric Titrations" (New York), 1926, 225; Vellinger, *Chimie et Industrie*, 1933, Special No., June, 218; *Ann. combustible liquides*, 1934, 9, 673; Parkes and Beard, *J. Phys. Chem.*, 1933, 37, 821; Bodforso and Holmquist, *Zeitsch. physikal. Chem.*, 1932, 161, 61; Catenacci, *L'Ind. sacc. Ital.*, 1931, 24, No. 8; *Int. Sugar J.*, 1932, 34, 185; Roche and Roche, *Arch. phys. biol.*, 1932, 9, 273; King, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 323; Leclerc, *Bull. assoc. ing. elec. (Liège)*, 1932, 10, 210; Uemura and Sueda, *Bull. Chem. Soc. Japan*, 1933, 8, 1; Hibbard, *J. Assoc. Official Agr. Chem.*, 1933, 16, 193; Gysinck, *Archiv. Suiker-ind. Nederl.-Indie*, 1932, [3], Med. 10, 711.

⁵ Britton and Robinson, *J. Chem. Soc.*, 1931, 134, 458; Kolthoff and Furman, *loc. cit.*; Catenacci, *loc. cit.*; Gex, *Arch. phys. biol.*, 1931, 9, 110; di Gléria, *Kisérlet. Kozlemények*, 1930, 33, 193; Itano, *loc. cit.*

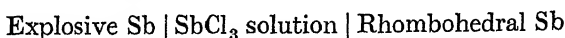
⁶ Parkes and Beard, *J. Amer. Chem. Soc.*, 1932, 54, 856. (These authors quote results obtained by other investigators.)

soils of varying pH value,¹ while the pH value against a standard calomel electrode varies according to the following : ²

$$pH = \frac{E + 0.026 + (t^\circ - 18)0.00016}{0.0542 + (t^\circ - 18)0.000275}$$

The electrode gives a linear relation between the observed e.m.f. and the pH values ³ with a probable error of 0.01 to 0.08 pH.⁴ It compares satisfactorily with the hydrogen and the quinhydrone electrodes,⁵ and has been recommended for use in connection with the examination of acids and alkalis, soils, blood, sugar liquors, etc.⁶ It does not appear to be suitable for use in connection with the leather industry.⁷

The e.m.f. of the cell :



is 0.014 volt, the temperature coefficient $\frac{dE}{dT}$ being 6.8×10^{-5} volt per degree. If the current exceeds a certain limiting value the cell explodes.⁸

Antimony exhibits the valve effect in nearly all electrolytes even at 600 to 700 volts.⁹ This is due to the formation of a layer of oxide on the surface of the anode.

The potential difference between antimony and air ¹⁰ is 0.16 volt.

Atomic Weight of Antimony.

Approximate Atomic Weight.—That the atomic weight of antimony is approximately 122, and not a multiple or submultiple of this amount, is indicated by several considerations :

The specific heat of antimony between 0 and 100° C. averages 0.05 calorie. Assuming a mean atomic heat of 6.4, the atomic weight, according to Dulong and Petit's Law, is approximately 128.

The properties of antimony indicate that the most appropriate position in the Periodic Table for this element lies immediately below arsenic, in the fifth group. This places it between tin (At. wt. 118.7) and tellurium (At. wt. 127.61), so that its atomic weight should lie between these values.

The atomic number of antimony, namely 51, confirms its position between tin (At. No. 50) and tellurium (At. No. 52).

¹ du Toit, *S. African J. Science*, 1930, 27, 227.

² Avseevitch and Shukov, *J. Gen. Chem. Russ.*, 1931, 1, 199; *Zeitsch. Elektrochem.*, 1931, 37, 771.

³ Fosbinder, *J. Lab. Clin. Med.*, 1931, 16, 411; Itano, *loc. cit.*; King, *Ind. Eng. Chem. (Anal.)*, 1933, 5, 323. See, however, di Gléria, *loc. cit.*

⁴ Gex, *loc. cit.*; Galvez, *Philippine Agr.*, 1930, 19, 219; Fosbinder, *loc. cit.*

⁵ Itano and Arakawa, *Ber. Ohara Inst. landw. Forsch. Japan*, 1930, [4], No. 3, 383; Verain and Mlle. Toussaint, *Compt. rend. soc. biol.*, 1930, 103, 611; Britton and Robinson, *loc. cit.*

⁶ Böttger and von Szebellédy, *Zeitsch. Elektrochem.*, 1932, 38, 737; *Amer. Dyestuff Repr.*, 1932, 21, 432; Houghoudt, *Verslag. landb. Onderzoek. Rijkslandbouwproefsta.*, 1930, 35, 162; Barnes and Simon, *J. Amer. Soc. Agron.*, 1932, 24, 156, Lakshmanrow, *Current Science*, 1932, 1, 34; Shukov and Bultunov, *J. Gen. Chem. Russ.*, 1932, 2, 407; du Toit, *loc. cit.*; Shukov and Gortikov, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 2055; *Zeitsch. Elektrochem.*, 1930, 35, 853.

⁷ Pleass, *Arch. phys. biol.*, 1932, 9, 267.

⁸ von Steinwehr and Schulze, *Zeitsch. Physik*, 1930, 63, 815.

⁹ Schulze, *Ann. Physik*, 1907, [4], 24, 43.

¹⁰ Andauer, *Zeitsch. physikal. Chem.*, 1928, 138 A, 357.

Application of Avogadro's hypothesis to the results of vapour density determinations of volatile antimony compounds indicates that the atomic weight of antimony is approximately 122.

The mass spectrum of antimony consists of two strong lines, 121 and 123 respectively, so that the atomic weight of the element must lie between these two values (see p. 38).

Exact Atomic Weight.—The dissatisfaction expressed by Berzelius in the words "*Ich habe niemals mit einer Materie, wo es so ausserordentlich schwer gewesen ist, konstante Resultate zu erhalten, gearbeitet*" has been experienced by many workers on the atomic weight of antimony, and few elements have proved so troublesome in this respect. It is only during the last few years that consistent values have been obtained; therefore, in the accompanying table, it will suffice merely to mention in most cases the mean results of the earlier researches. All the atomic weight values have been recalculated from the ratios given, using in addition to the antecedent data quoted in the Introduction, p. x, the following values: Cu, 63.57; Ba, 137.6.

Of the researches prior to 1921, those of Cooke alone need be mentioned.

Cooke¹ attempted to exercise the same care in his work as Stas had done in his classical determinations. He worked, however, with small quantities, whereas Stas sometimes used more than 100 grams. Cooke therefore reduced the error due to occlusion of solution by the precipitate by employing much more dilute solutions. In his initial work he employed four methods.

(a) *Synthesis of Antimony Trisulphide.*—Balls of antimony were treated with hydrochloric acid containing a little nitric acid, and the solution boiled until it became colourless. The balls were then removed, washed, dried and weighed; the loss in weight gave the amount of antimony dissolved. The solution was diluted with aqueous tartaric acid, and antimony trisulphide precipitated by means of water saturated with hydrogen sulphide. The washed precipitate was dried at 130° C. The analysis of this gave $2\text{Sb} : 3\text{S} = 71.4269 : 28.5781$, whence $\text{Sb} = 120.22$. On heating to 210° the red trisulphide changed into the black variety. This gave the ratio $2\text{Sb} : 3\text{S} = 71.4818 : 28.5182$; whence $\text{Sb} = 120.56$.

(b) *Analysis of Antimony Trichloride.*—The material was purified by distillation and by crystallisation from carbon disulphide. The analysis was carried out by dissolving the trichloride in aqueous tartaric acid and adding silver nitrate solution. The ratio $\text{SbCl}_3 : 3\text{AgCl} = 53.066 : 100$ gives a value for antimony, 121.82, almost identical with that obtained by Dumas, using the same method. Cooke, however, was not satisfied with the result since it did not agree with certain of his other determinations. He advanced the suggestion that the high result was due to the presence of some oxychloride in the trichloride; this, however, is not supported by the evidence of his own work.

(c) *Analysis of Antimony Tribromide.*—The tribromide was prepared by the action of powdered metallic antimony upon bromine in carbon disulphide solution. It was purified by distillation over finely powdered antimony and crystallised from carbon disulphide. The ratio $\text{SbBr}_3 : 3\text{AgBr} = 63.830 : 100$ gave $\text{Sb} = 119.868$.

¹ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 1; 1880, 15, 251; 1881, 17, 1; *Ber.*, 1880, 13, 951.

DETERMINATIONS OF THE ATOMIC WEIGHT OF ANTIMONY.

Authority.	Ratio Determined.	No. of Expts.	Atomic Weight of Antimony.
Berzelius ¹ (1812) .	2Sb : Sb ₂ O ₄ = 100 : 124.8	..	129.0
Kessler ² (1855-1860) .	Various methods from which he deduced the mean value	122.37
Schneider ³ (1856) .	2Sb : 3S = 71.480 : 28.520	8	120.55
Weber ⁴ (1856) .	One analysis of SbCl ₃	1	120.7
Dexter ⁵ (1857) .	2Sb : Sb ₂ O ₄ = 79.283 : 100	13	122.46
Dumas ⁶ (1859) .	SbCl ₃ : 3Ag = 70.512 : 100	7	121.83
Unger ⁷ (1871) .	Analysis of Schlippe's Salt, Na ₃ SbS ₄ .9H ₂ O	1	119.8
Cooke ⁸ (1877) .	2Sb : 3S = 71.4818 : 28.5182	11	120.56
	SbCl ₃ : 3AgCl = 53.066 : 100	17	121.82
	SbBr ₃ : 3AgBr = 63.830 : 100	15	119.863
	SbI ₃ : 3AgI = 71.060 : 100	7	119.786
Cooke ⁹ (1880-1881) .	SbBr ₃ : 3Ag = 111.114 : 100	5	119.861
Schneider ¹⁰ (1880) .	2Sb : 3S = 71.459 : 28.541	3	120.42
Pfeifer ¹¹ (1881) .	3Cu : 2Sb = 100 : 128.259	3	122.23
	3Ag : Sb = 100 : 37.485	7	121.32
Bongartz ¹² (1883) .	2Sb : 3BaSO ₄ = 100 : 290.306	12	120.62
Popper ¹³ (1886) .	3Ag : Sb = 100 : 37.434	15	121.15
Friend and Smith ¹⁴ (1901)	C ₆ H ₄ KSbO ₇ : KCl = 100 : 23.0484	8	120.34
Willard and McAlpine ¹⁵ (1921)	SbBr ₃ : 3AgBr = 35.69757 : 55.63121	8	121.768
Muzaffar ¹⁶ (1923) .	3SbCl ₃ : KBrO ₃ (see p. 37)	32	{ 121.138 to 122.400 122.06 121.76 121.76 121.748 121.716 to 121.758
Knop ¹⁷ (1923) .	2Sb : Sb ₂ O ₄ = 2.7250 : 3.4395	6	
Honigschmid, etc. ¹⁸ (1924)	SbCl ₃ : 3Ag = 70.488 : 100	8	
	SbBr ₃ : 3Ag = 111.699 : 100	8	
Weatherill ¹⁹ (1924) .	SbCl ₃ : 3Ag = 100 : 70.4864	8	
Krishnaswami ²⁰ (1927)	SbBr ₃ : 3Ag (see p. 37)	21	

¹ Berzelius, *Afhandlingar i Fysik, Kemi, etc.*, V, 490; *K. Vet. Akad. Handl.*, 1812, 189; *Gilbert's Annalen*, 1812, 42, 283; *Schweigger's J.*, 1812, 6, 155; 1818, 22, 70; 1818, 23, 200. *Pogg. Annalen*, 1826, 8, 1.

² Kessler, *Pogg. Annalen*, 1855, 95, 204; 1860, 113, 134.

³ Schneider, *Annalen*, 1856, 97, 483; 1856, 98, 293.

⁴ Weber. See Rose, *Annalen*, 1856, 98, 455.

⁵ Dexter, *Annalen*, 1857, 100, 563.

⁶ Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 175.

⁷ Unger, *Archiv Pharm.*, 1871, 197, 194.

^{8, 9} Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 1; 1880, 15, 251; *Ber.*, 1880, 13, 951.

¹⁰ Schneider, *J. prakt. Chem.*, 1880, [2], 22, 131.

¹¹ Pfeifer, *Annalen*, 1881, 209, 174. (Electrochemical method.)

¹² Bongartz, *Ber.*, 1883, 16, 1942.

¹³ Popper, *Annalen*, 1886, 233, 153. (Electrochemical method.)

¹⁴ G. C. Friend and E. F. Smith, *J. Amer. Chem. Soc.*, 1901, 23, 502.

¹⁵ Willard and McAlpine, *ibid.*, 1921, 43, 797.

¹⁶ Muzaffar, *ibid.*, 1923, 45, 2009.

¹⁷ Knop, *Zeitsch. anal. Chem.*, 1923, 63, 181.

¹⁸ Honigschmid, Zintl and Linhard, *Zeitsch. anorg. Chem.*, 1924, 136, 257.

¹⁹ Weatherill, *J. Amer. Chem. Soc.*, 1924, 46, 2437.

²⁰ Krishnaswami, *J. Chem. Soc.*, 1927, p. 2534.

(d) *Analysis of Antimony Triiodide*.—The analysis was carried out in the same way as those of the tribromide and trichloride. The ratio $\text{SbI}_3 : 3\text{AgI} = 71.060 : 100$ gave $\text{Sb} = 119.786$.

In the years 1880 and 1881 Cooke carried out his final determinations using antimony tribromide. The material was repeatedly distilled from metallic antimony, recrystallised several times from carbon disulphide, subjected to repeated fractional distillation, and finally twice sublimed in a current of carbon dioxide. It is probable that Cooke would have obtained better results had his process of purification been less prolonged. Working without modern refinements in the handling of highly hygroscopic materials, the introduction of a trace of moisture was inevitable; thus the carbon dioxide, though described as absolutely dry, was only subjected to the action of calcium chloride and sulphuric acid. It is clear, therefore, that the resublimed product was much more likely to contain hydrogen bromide than antimony oxybromide, the impurity which Cooke feared. Willard and McAlpine,¹ as a result of a critical study of Cooke's papers, consider that his material may have contained as much as 1 per cent. of hydrogen bromide.

Turning now to the values given in the table (p. 34), it will be observed that, with certain early exceptions, the values recorded fall into two groups, those approximating to 120 and 122 respectively. On the basis of the work of Kessler, Dexter and Dumas the value 122 was adopted, although Schneider's results pointed to the lower value. After the laborious investigation carried out by Cooke, which gave results of such striking concordance, the number 120 was immediately adopted. The electrochemical studies of Pfeifer and Popper indicated the higher value once more, but so great was the prejudice in favour of Cooke's work that no alteration was made; moreover the electrochemical work was adversely criticised by Cohen, Collins and Strengers,² on the ground that the method did not give constant results. The work of Friend and Smith, however, indicated that Cooke's results were somewhat too low, so that after 1902 the number 120.2 was adopted; an unjustifiable compromise which was obviously unsatisfactory. The controversy continued; certain workers on antimony appeared to find the value 120.2 satisfactory.³ Others, however, obtained results pointing to the higher value,⁴ and expressed the opinion that the older value, 122, was the more correct.

The insecurity of the basis for the atomic weight led Willard and McAlpine in 1921 to reinvestigate the whole question.⁵ They prepared pure antimony tribromide with careful exclusion of moisture. In an all-glass apparatus, three different preparations of antimony were combined with bromine, the product twice distilled at a pressure of 5 to 10 mm., then distilled a third time at less than 1 mm. into a series of small bulbs which were sealed off from each other as individual

¹ Willard and McAlpine, *J. Amer. Chem. Soc.*, 1921, 43, 817.

² Cohen, Collins and Strengers, *Zeitsch. physikal. Chem.*, 1904, 50, 308.

³ Henz, *Zeitsch. anorg. Chem.*, 1903, 37, 6; Vortmann and Metzl, *Zeitsch. anal. Chem.*, 1905, 44, 528; Kolb and Formhals, *Zeitsch. anorg. Chem.*, 1908, 58, 189; Hallmann, *Vergleichende Untersuchungen und Methoden der quant. Antimonbestimmung*, Inaugural Dissertation, Aachen, 1911.

⁴ Youtz, *Zeitsch. anorg. Chem.*, 1903, 37, 337; Beckett, *Beitrag Best. Antimons*, Inaugural Dissertation, Zurich, 1909; de Bacho, *Monatsh.*, 1916, 37, 106; Treadwell, *Kurzes Lehrbuch anal. Chem.*, 5th ed., 2, 563.

⁵ Willard and McAlpine, *J. Amer. Chem. Soc.*, 1921, 43, 797.

samples. From the time the pure dry materials were placed in the apparatus until the bulbs were broken under tartaric acid solution, only inert gases came into contact with the preparation. The resulting product was analysed for bromine in two ways: first, volumetrically, by finding the amount of silver, dissolved in nitric acid, equivalent to the sample, using a nephelometric end point; second, gravimetrically, by adding excess of silver nitrate, then filtering out and weighing the silver bromide. The precautions taken and corrections applied included all those which had been described within recent years on similar work. In eight of the best volumetric analyses, a total of 35.69757 grams of antimony bromide formed 55.63121 grams of silver bromide, from which the atomic weight of antimony is 121.768. By taking into consideration the three slightly less satisfactory volumetric analyses, and eight gravimetric analyses, Willard and McAlpine gave the mean value 121.773. The former value, however, is the more trustworthy and has therefore been included in the table.

Knop¹ obtained an appreciably higher value. He treated pure antimony with nitric acid and converted the product into the tetroxide by ignition at 850° to 900° C., at which temperature the pentoxide is fully reduced to the tetroxide, but the latter is not further reduced. The purity of the product was established by the iodine-thiosulphate method. The results gave a mean value $Sb = 122.06$, or 121.96 when reduced to vacuum.*

Hönigschmid, Zintl and Linhard² hydrolysed chloroantimonic acid, $HSbCl_6 \cdot 4.5H_2O$ (prepared from antimony pentasulphide) and reduced the resulting antimonious acid in hydrogen at 500° C. The metal was converted into the chloride or bromide by heating in a current of the halogen, and the halides fractionally distilled, first in pure nitrogen and then in a vacuum. The silver equivalent of each halide was determined by gravimetric titration and weighing the silver halide formed. The mean of thirty-two very concordant results gave $Sb = 121.76$.

Weatherill³ applied Willard and McAlpine's method to the trichloride. Kahlbaum's purest antimony was twice fused in hydrogen, combined with pure chlorine, and the product repeatedly distilled in an evacuated glass apparatus, considerable head and tail fractions being rejected in each distillation. The mean of 8 analyses gave the ratio $SbCl_3 : 3Ag$ as 0.704864, from which the atomic weight of antimony is 121.748. This is slightly lower than the values obtained by Willard and McAlpine, and by Hönigschmid, but agrees remarkably well with that of Krishnaswami (see below).

The discovery of non-radioactive isotopes of certain elements has taught that elements from different localities may conceivably possess their constituent isotopes in different proportions, so that their atomic weights may vary. A review of the earlier work on the atomic weight of antimony led Muzaffar⁴ to inquire whether or not such might be the case with this element. Stibnite was obtained from Peru, Bolivia, Borneo and Hungary. After purifying all samples by the same method,

¹ Knop, *Zeitsch. anal. Chem.*, 1923, 63, 181.

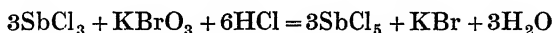
* Knop gives the mean values of 122.04 and 121.94 respectively. The above values are calculated from the ratio given in the table, which gives the total weights of antimony and its oxide handled in the six experiments.

² Hönigschmid, Zintl and Linhard, *Zeitsch. anorg. Chem.*, 1924, 136, 257.

³ Weatherill, *J. Amer. Chem. Soc.*, 1924, 46, 2437.

⁴ Muzaffar, *J. Amer. Chem. Soc.*, 1923, 45, 2009.

the antimony was converted into trichloride and the ratio between antimony trichloride and potassium bromate determined by titration :



The results were as follows :

Source of Stibnite.	Ratio 3Sb : KBrO ₃ .	No. of Experiments.	Atomic Weight of Antimony.
Hungary .	2.17592	7	121.138
Borneo .	2.1836	7	121.565
Peru .	2.1862	7	121.710
Bolivia .	2.1986	11	122.400

Excellent concordance was obtained in the first set of results using Hungarian material, and the low value for the atomic weight is remarkable.

More recently ¹ specimens of stibnite have been obtained from the same sources as those used by Muzaffar. The metal was extracted, and the densities compared with that of a specimen of Kahlbaum's antimony. In addition, solutions were titrated with solutions of potassium bromate and the ratio KBrO₃/3Sb was determined. It was found that the densities of the specimens were all within 0.1 per cent. of each other ; and that the ratios KBrO₃/3Sb agreed to 0.05 per cent. The evidence of variation in the atomic weight of antimony from different sources does not therefore appear to have been confirmed.

Krishnaswami ² directed attention to certain disadvantages occurring in practice when Muzaffar's method is adopted, and gave the results of determining the atomic weight of antimony from four ores of Indian and Burmese origin, using Willard and McAlpine's method in its entirety. His results were as follows :

Source of Material.	Ratio SbBr ₃ : 3AgBr.	No. of Experiments.	Atomic Weight of Antimony.
Kahlbaum's Sb ₂ O ₃ .	0.641664	6	121.758
Mysore stibnite .	0.641647	4	121.748
Mysore cervantite .	0.641647	3	121.748
Amherst stibnite .	0.641652	5	121.751
Shan States stibnite .	0.64159	3	121.716

A close agreement between the values from the Mysore stibnite and cervantite was of course to be expected since the latter is an alteration product of the former. The results do not indicate any appreciable difference between the samples.

¹ McAlpine, *J. Amer. Chem. Soc.*, 1929, 51, 1745.

² Krishnaswami, *J. Chem. Soc.*, 1927, p. 2534.

The International Committee on Atomic Weights for 1936 has adopted the value

$$\text{Sb} = 121.76$$

The Council of the Chemical Society had, in 1919, recommended this value and it has been retained until the present time (1936).

Isotopes.—Two isotopes of antimony have been discovered, with atomic masses 121 and 123. The ratio $\text{Sb}^{121} : \text{Sb}^{123}$ is provisionally given as 100 : 78.5, thus indicating a mean mass of 121.88 and an isotopic moment of 0.96. Though the packing fraction has not been determined, it is assumed to lie between those of tin and xenon, and on this assumption the calculated atomic weight is 121.79, which compares very favourably with the value obtained by chemical methods.¹ Owing to the unsuitability of antimony trihydride for the determination of the isotopic constitution, antimony methyl has been employed in the more recent work. A nuclear moment² of $5/2$ has been assigned to Sb^{121} , and one of $7/2$ to Sb^{123} . The atomic radius³ calculated from the structure of antimony tribromide is 1.25 Å., and from antimony trichloride, 1.21 Å. An inner potential⁴ of 12 volts has been deduced from the refraction due to the reflection of high-speed electrons from cleavage faces of antimony.

From the fluorescence of antimony excited by several mercury lines, the value 2.21 Å. has been obtained for the nuclear separation in diatomic molecules, and the value 489×10^{-40} gram-cm.² for the moment of inertia.⁵

Alloys of Antimony.

Antimony enters into the composition of a large number of commercial alloys, including antimonial lead (lead containing up to 4 per cent. of antimony) which is used for the framework of accumulator plates, lead shot (in which antimony replaces the more usual alloying element arsenic), lead anodes for chromium plating and other purposes, type metal (consisting of alloys of lead, antimony, tin and sometimes copper), Britannia metal and pewter (alloys of tin, antimony, lead and sometimes copper and bismuth), and antifriction metals, such as Babbitt metal (a wide range of alloys, a number of which contain tin, lead, antimony and copper).⁶ In general, antimony acts as a hardening metal, and excess is liable to induce brittleness. It has been stated that alloys of antimony with iron and certain other metals are resistant to acid.⁷

A number of alloy systems with antimony as one of the components has been examined thermally and microscopically, by means of X-rays,

¹ Aston, *Proc. Roy. Soc.*, 1931, 132 A, 492; *Phil. Mag.*, 1923, [6], 45, 943; *Nature*, 1922, 110, 732.

² Badami, *Nature*, 1932, 130, 697; *Zeitsch. Physik*, 1932, 79, 206. See also Tolansky, *Proc. Roy. Soc.*, 1934, 146 A, 182; Crawford and Bateson, *Canad. J. Research*, 1934, 10, 693.

³ Bergmann and Engel, *J. Physical Chem.*, 1931, 13 B, 247. See also Goldschmidt, *Zeitsch. physikal. Chem.*, 1928, 133, 397.

⁴ Darbyshire, *Phil. Mag.*, 1933, 16, 761.

⁵ Genard, *Phys. Review*, 1933, [2], 44, 468. See also Sen, *Zeitsch. anorg. Chem.*, 1933, 212, 410.

⁶ Roekaert, *Aciers speciaux*, 1929, 4, 470.

⁷ Frischer, *French Patent*, 1931, 725448.

and by the correlation of physical properties with composition. The bibliographies which accompany these brief accounts deal mainly with the physico-chemical constitution of the alloys; references to method of manufacture, treatment, working or uses of the alloys have not, in general, been included.¹

Antimony-Sodium Alloys.²—Two compounds are formed, Na_3Sb (M.pt. 823°C.) and NaSb (M.pt. 503°C.), which enter into the formation of three eutectics, at 0.5 per cent. antimony (M.pt. 95°C.), 80 per cent. antimony (M.pt. 430°C.), and 90.6 per cent. antimony (M.pt. 404°C.). There is no range of solid solution. The e.m.f.s. of these alloys have also been investigated.³ Substances of the composition Na_3Sb_7 , $\text{Na}_3\text{Sb}_7\cdot\text{NH}_3$ and $\text{Na}_3\text{Sb}_7\cdot 6\text{NH}_3$ have been obtained by extracting an alloy of sodium and antimony with liquid ammonia.⁴

Antimony-Potassium Alloys.⁵—Two compounds are formed, K_3Sb (M.pt. 812°C.) and KSb (M.pt. 605°C.), which enter into the formation of three eutectics melting at 63°C. , 400°C. and 485°C. respectively.

Antimony-Copper Alloys.⁶—Two definite compounds are formed: Cu_5Sb_2 (M.pt. 680°C.) and Cu_2Sb (decomposing at 580°C.); it is possible that a third compound, Cu_3Sb , may exist below 430°C. There are two eutectics, namely at 23 per cent. copper (M.pt. 535°C.) and 72 per cent. copper (M.pt. 634°C.). Copper forms a solid solution in antimony up to 1.2 per cent., and antimony dissolves in copper up to 7 per cent. Transformations in the solid state occur at 430°C. (when the compound Cu_5Sb_2 undergoes decomposition), and in copper-rich alloys at 450°C. Other physical properties that have been examined are the heats of mixing,⁷ which at $1,200^\circ\text{C.}$ reach a maximum of +903 gram-calories at 57.4 atomic per cent. copper, and variations in e.m.f.⁸ X-ray examinations of this system have been carried out.⁹

Antimony-Silver Alloys.¹⁰—One compound, Ag_3Sb , is formed, decomposing at 560°C. , and one eutectic containing 55 per cent. silver (M.pt. 482°C.). The solid solubility of antimony in silver is 6 per cent.; silver appears to be insoluble in antimony in the solid state. The heat of mixing (at $1,050^\circ\text{C.}$) rises to a maximum of +1,192 gram-calories at 71.6 atomic per cent. silver.¹¹

¹ Constitutional diagrams of many of the systems cited will be found in *International Critical Tables*, 1927, 2, 401–427.

² Mathewson, *Zeitsch. anorg. Chem.*, 1906, 50, 171; Peck, *J. Amer. Chem. Soc.*, 1918, 40, 335.

³ Kremann and Pfeiderer, *Zeitsch. Metallkunde*, 1921, 13, 19.

⁴ Zintl and Harder, *Zeitsch. physikal. Chem.*, 1932, B 16, 183, 206.

⁵ Parravano, *Gazzetta*, 1915, 45, i, 485.

⁶ Carpenter, *Zeitsch. Metallkunde*, 1913, 4, 300; Heycock and Neville, *Phil. Trans.*, 1897, A 189, 25; Reimann, *Zeitsch. Metallkunde*, 1920, 12, 321; Parravano and Viviani, *Atti R. Accad. Lincei*, 1910, [5], 19, i, 197, 243, 343, 835; ii, 69; Hume-Rothery, Mabbott and Channel Evans, *Phil. Trans.*, 1934, 233 A, 1; Archbutt and Prytherch, *J. Inst. Met.*, 1931, 45, 265.

⁷ Kawakami, *Science Reports Tohoku Imp. Univ.*, 1930, 19, 521.

⁸ Pace, *Gazz. chem. ital.*, 1930, 60, 811.

⁹ Howells and Morris Jones, *Phil. Mag.*, 1930, [7], 9, 993; Westgren, Hågg and Eriksson, *Zeitsch. physikal. Chem.*, 1929, B 4, 453; Morris Jones and Evans, *Phil. Mag.*, 1927, [7], 4, 1302.

¹⁰ Petrenko, *Zeitsch. anorg. Chem.*, 1906, 50, 133; Kremann and Bayer, *Monatsh.*, 1926, 46, 649. For X-ray examination, see Broderick and Ehret, *J. Phys. Chem.*, 1931, 35, 2627.

¹¹ Kawakami, *loc. cit.*

Antimony-Gold Alloys.¹—One compound, AuSb_2 ,² is formed, which exists in three modifications with transition points at 355.2°C. and 405°C. ; it probably decomposes at 460°C. There is a maximum on the liquidus curve at 55 per cent. gold (492°C.) and two eutectics occur, namely at 46 per cent. gold (M.pt. 480°C.) and at 75 per cent. gold (M.pt. 370°C.). There appears to be no range of solid solution. Electrical conductivity curves agree with the results of thermal analysis.³

Antimony-Magnesium Alloys.⁴—One compound, Mg_3Sb_2 (M.pt. $1,228^\circ \text{C.}$) is known, which forms two eutectics, at 86 atomic per cent. antimony (M.pt. 579°C.) and 10 atomic per cent. antimony (M.pt. 629°C.). The compound Mg_3Sb_2 undergoes a transformation at 930°C. and enters into solid solution with magnesium. The temperature of the transformation falls slightly throughout the range of solid solubility.

Antimony-Calcium Alloys.⁵—Only the antimony-rich alloys appear to have been studied. There is a eutectic at 8 per cent. calcium (M.pt. 585°C.).

Antimony-Zinc Alloys.⁶—Two compounds are formed, Zn_3Sb_2 (M.pt. 568°C.) and ZnSb (decomposing at 534°C.), forming two eutectics at 1.7 per cent. antimony (M.pt. 412°C.) and at 80 per cent. antimony (M.pt. 505°C.). At room temperature the compound Zn_3Sb_2 decomposes into metallic zinc and the compound ZnSb . A discontinuity in the curve for the magnetic susceptibility⁷ indicates the formation of the compound ZnSb , which has also been examined by X-rays.

Antimony-Cadmium Alloys.⁸—It is probable that two compounds are formed,⁹ Cd_3Sb_2 (decomposing at 410°C.) and CdSb (M.pt. 455°C.), although the existence of the former has been queried.¹⁰ Three other compounds have been indicated¹¹ for which the following formulæ have been proposed: Cd_5Sb_3 , Cd_4Sb_5 and Cd_5Sb_5 . There are two eutectics, at 40 per cent. cadmium (M.pt. 445°C.) and 93 per cent. cadmium (M.pt. 290°C.). The magnetic susceptibility has been studied,¹² while the heat of mixture (at 800°C.) shows a maximum of +829 gram-calories at 46.7 atomic per cent. antimony.

¹ Vogel, *Zeitsch. anorg. Chem.*, 1906, 50, 145; Grigoriev, *Ann. Inst. Platine*, 1929, 7, 32. For X-ray examination, see Niall, Almin and Westgren, *Zeitsch. physikal. Chem.*, 1931, B 14, 81.

² Bottema and Jaeger, *Proc. Acad. Sci. Amsterdam*, 1932, 35, 916, 929; *Rec. Trav. chim.*, 1933, 52, 89.

³ Grigoriev, *Zeitsch. anorg. Chem.*, 1932, 209, 289.

⁴ Grube and Bornhak, *Zeitsch. Elektrochem.*, 1934, 40, 140; Leitgeb, *Zeitsch. anorg. Chem.*, 1931, 202, 305; Grube, *ibid.*, 1906, 49, 72.

⁵ Donski, *Zeitsch. anorg. Chem.*, 1908, 57, 185.

⁶ Zhemchuzhnyi, *Zeitsch. anorg. Chem.*, 1913, 4, 228; Kremann, Ortner and Markl, *Monatsh.*, 1924, 44, 401; Sauerwald, *Zeitsch. Metallkunde*, 1922, 14, 457. For X-ray examination, see Halla, Nowotny and Tompa, *Zeitsch. anorg. Chem.*, 1933, 214, 196.

⁷ Meara, *Physics*, 1932, 2, 33.

⁸ Kurnakov and Konstantinov, *Zeitsch. anorg. Chem.*, 1908, 58, 1; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 227; Kremann and Gmachl-Pammer, *Intern. Zeitsch. Metallographie*, 1920, 12, 241; Fischer and Pfeiderer, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 440; Eucken and Gehloff, *Ber. deut. physikal. Ges.*, 1912, 14, 169.

⁹ Halla, Nowotny and Tompa, *Zeitsch. anorg. Chem.*, 1933, 214, 196; Halla and Adler, *Zeitsch. anorg. Chem.*, 1929, 185, 184.

¹⁰ Chikashige and Yamamoto, "Anniversary Volume," *Kyoto Imp. Univ.*, 1930, 195; Abel, Redlich and Adler, *Zeitsch. anorg. Chem.*, 1928, 174, 257; Abel, Adler, Halla and Redlich, *Zeitsch. anorg. Chem.*, 1932, 205, 398.

¹¹ Volfsen and Roshdestvenski, *J. Exp. Theor. Phys.*, U.S.S.R., 1933, 3, 447.

¹² Meara, *loc. cit.*

Antimony-Aluminium Alloys.¹—It is difficult to obtain equilibrium with these alloys. The solid solubility of antimony in aluminium is less than 0.10 per cent. at 645° C.; a eutectic is formed at 1.1 per cent. antimony (657° C.) and a maximum on the liquidus curve at 1,080° C. corresponds to the compound AlSb. The liquidus curve shows another maximum at 32 per cent. antimony (984° C.) and a minimum at 35 per cent. antimony (942° C.) There appear to be two eutectics. The compound AlSb decomposes in moist air, aluminium hydroxide being formed.

Antimony-Thallium Alloys.²—One compound is formed, Tl₃Sb (decomposing at 187° C.), which gives solid solutions with thallium but not with antimony. A eutectic is formed at 19 per cent. antimony (M.pt. 196° C.), while the thallium-rich alloys undergo a transformation (probably connected with the allotropy of thallium) at 226° C. Another compound, Tl₇Sb₂, has also been reported.³

Antimony-Silicon Alloys.⁴—Antimony and silicon show only slight solid solubility; the eutectic melts at 630° C. No compounds are formed.

Antimony-Tin Alloys.⁵—This system is complex, a number of solid solutions being formed. There are two compounds, SnSb (decomposing at 427° C.) and Sn₃Sb₂ (decomposing at 819° C.). A transformation occurs in the range 30 to 70 per cent. antimony, which is connected with a polymorphic change in the β -solid solution. An X-ray examination of these alloys has been made, and it is suggested that the compound SnSb has the structure of a simple cube of the KCl type—a very unusual structure for an intermetallic compound.⁶ The unit cell contains 4 molecules, with $a = 6.120$ Å. The more usual structure of a body-centred cube, with $a = 6.13$ Å. has, however, also been proposed for this compound,⁷ and further, as the result of a more recent investigation, the structure has been described as of the KCl type, but deformed.⁸ This compound is also unusual in dissolving both antimony and tin. The existence of the compound SnSb is also indicated on the curve of magnetic susceptibility.⁹

Antimony-Lead Alloys.¹⁰—These metals form a eutectiferous

¹ Veszelka, *Mitt. berg.-hüttenmänn. Abt. ungar. Hochschule Berg.-Fortsw. Sopron*, 1931, 3, 193; *Chem. Zentr.*, 1932, i, 2230; Bonaretti, "Metalli leggieri," 1931, 29; Dix, Keller and Willey, *Amer. Inst. Mining Eng.*, 1930, Tech. Pub. No. 356; Campbell and Matthews, *J. Amer. Chem. Soc.*, 1902, 24, 253; Kremann and Dellacher, *Monatsh.*, 1926, 46, 547; Sauerwald, *loc. cit.*; Guertler and Bergmann, *Zeitsch. Metallkunde*, 1933, 25, 81, 111.

² Winogorov and Petrenko, *Zeitsch. anorg. Chem.*, 1926, 150, 258; Kremann and Lobinger, *Intern. Zeitsch. Metallographie*, 1920, 12, 246; *Chem. Zentr.*, 1921, i, 123; Bekier, *Chemik Polski*, 1917, 15, 119; *Chem. Zentr.*, 1918, i, 1000; Williams, *Zeitsch. anorg. Chem.*, 1907, 55, 1.

³ Morrall and Westgren, *Svensk Kem. Tidskr.*, 1934, 46, 153.

⁴ Jette and Gebert, *J. Chem. Physics*, 1933, 1, 753; Williams, *loc. cit.*

⁵ Iwasi, Aoki and Osawa, *Science Reports Tohoku Imp. Univ.*, 1931, [1], 20, 353; *Kinzoku-no-Kenkyu* (J. for Study of Metals), 1930, 7, 147; Guertler, "Metallographie," 1910; Williams, *loc. cit.*; Leroux, *Compt. rend.*, 1913, 156, 1764; Konstantinov and Smirnov, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1201.

⁶ Morris Jones and Bowen, *Nature*, 1930, 126, 846; *Phil. Mag.*, 1931, 12, 441; van Klooster and Debacher, *Metals and Alloys*, 1933, 4, 23; Iwasi, Aoki and Osawa, *loc. cit.*

⁷ von Schwarz and Summa, *Zeitsch. Metallkunde*, 1933, 25, 95.

⁸ Hägg and Hybinette, *Phil. Mag.*, 1935, [7], 20, 913.

⁹ Meara, *Physics*, 1932, 2, 33.

¹⁰ Dean, Hudson and Fogler, *Industrial and Engineering Chemistry*, 1925, 17, 1246; Fischer, *Zeitsch. tech. Physik*, 1925, 6, 146; Gontermann, *Zeitsch. anorg. Chem.*, 1907, 55, 419; Dean, *J. Amer. Chem. Soc.*, 1923, 45, 1683; Muzaffar, *Trans. Faraday Soc.*, 1923, 19, 56; Leroux, *loc. cit.*; Stephens, *Phil. Mag.*, 1930, [7], 9, 547.

series of alloys with a eutectic at 87 per cent. lead (M.pt. 247° C.). A more recent examination of these alloys after very slow cooling suggests that the eutectic contains 11.4 to 11.5 per cent. antimony.¹ It is suggested that a compound Pb_2Sb is formed which is soluble in liquid antimony, and that it forms a solid solution in monatomic molecules of lead at all temperatures between 25° C. and the melting point of pure lead.² A maximum is found on the boiling point curve.³ The hardness⁴ and specific heats⁵ have been determined, the specific heat between 0° and 100° C. being given by the expression

$$s = 0.04965 - 0.0001884p$$

where p is the percentage of lead in the alloy. These alloys have been examined by X-rays,⁶ and from the results it is deduced that the solid solubility of antimony in lead cannot be more than 0.5 per cent. From electrical conductivity experiments⁷ it is concluded, however, that at 249° C. the solid solubility of lead in antimony is 5.8 atomic per cent., and that of antimony in lead is 1.5 atomic per cent.

Antimony-Arsenic Alloys.⁸—These elements form a continuous series of solid solutions up to 40 per cent. arsenic. There is a minimum on the liquidus curve at 17.5 per cent. arsenic (612° C.).

Antimony-Bismuth Alloys.⁹—These metals form a continuous series of solid solutions, the liquidus curve lying wholly between the melting points of the two metals, and the solidus being practically horizontal between 0 and 60 per cent. antimony. Some evidence for the existence of Bi_2 molecules has been obtained, and the anomalous form of the solidus curve has been ascribed to this.¹⁰ The hardness¹¹ has been determined. The boiling point curve shows a maximum.¹² These alloys have been examined by X-rays, homogeneity being obtained by prolonged annealing at 280° C. The lattice edge of the rhombohedral crystals varies almost linearly with composition.¹³

Antimony-Chromium Alloys.¹⁴—Two compounds are formed, $CrSb$ (M.pt. $1,110^{\circ}$ C.) and $CrSb_2$ (decomposing at 675° C.), and two eutectics, at 2 per cent. chromium (M.pt. 620° C.) and 38 per cent. chromium (M.pt. $1,100^{\circ}$ C.). Antimony is soluble in chromium to the extent of 12 per cent.

Antimony-Selenium Alloys.¹⁵—One compound, Se_3Sb_2 (M.pt.

¹ Quadrat and Jiriste, *Chim. et Ind.*, 1934, *Special Number* (April), 485.

² Jeffery, *Trans. Faraday Soc.*, 1932, 28, 567; see, however, Chu-Phay Yap, *Amer. Inst. Min. Met. Eng., Inst. Metals Division*, 1931.

³ Leitgeb, *Zeitsch. anorg. Chem.*, 1931, 202, 305.

⁴ Saposhnikov and Kanewsky, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 901.

⁵ Durrer, *Physikal. Zeitsch.*, 1918, 19, 86.

⁶ Solomon and Morris Jones, *Phil. Mag.*, 1930, [7], 10, 470; Obinata, *Metallwirtschaft*, 1933, 12, 101.

⁷ Le Blanc and Schöpel, *Zeitsch. Elektrochem.*, 1933, 39, 695.

⁸ Parravano and de Cesaris, *Intern. Zeitsch. Metallographie*, 1912, 2, 70.

⁹ Cook, *J. Inst. Metals*, 1922, 28, 421; Otani, *Sci. Rep. Tohoku Imp. Univ.*, 1925, 13, 293; Parravano and Viviani, *Atti R. Accad. Lincei*, 1910, [5], 19, i, 835; Ehret and Abramson, *J. Amer. Chem. Soc.*, 1934, 56, 385.

¹⁰ Chu-Phay Yap, *loc. cit.*

¹¹ Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 665.

¹² Leitgeb, *loc. cit.*

¹³ Bowen and Morris Jones, *Phil. Mag.*, 1932, [7], 13, 1029.

¹⁴ Williams, *loc. cit.*

¹⁵ Chikashige and Fujita, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1917, 2, 233; Parravano, *Gazzetta*, 1913, 43, i, 210.

570° C.) is formed, and two eutectics, at 47 per cent. selenium (M.pt. 493° C.) and at 99.7 per cent. selenium (M.pt. 210° C.).

Antimony-Tellurium Alloys.¹—These alloys are described as forming a series of "mixed crystals."

Antimony-Manganese Alloys.²—Three compounds have been described: MnSb (M.pt. 809° C.), Mn_3Sb_2 (decomposing at 872° C.) and Mn_2Sb (M.pt. 971° C.). Two eutectics are also formed, at 9.5 per cent. manganese (M.pt. 570° C.) and at 55 per cent. manganese (922° C.). Ranges of solid solution exist between 32 to 41 and 45 to 50 per cent. manganese. Some of the alloys show paramagnetism.

Antimony-Iron Alloys.³—Two compounds have been described, Fe_3Sb_2 (M.pt. 1015° C.) and FeSb_2 . There are two eutectics, at 50.5 per cent. antimony (M.pt. 1,002° C.) and at 92.5 per cent. antimony (M.pt. 628° C.). The eutectic range in the iron-rich alloys extends from 5 to 52 per cent. antimony, and throughout this range there is a transformation at 798° C. corresponding to the change from γ -iron to α -iron. The solid solubility of antimony in iron is reported to be 6.5 per cent.; X-ray examination, however,⁴ suggests that the solid solubility of antimony in iron is higher. There is also a range of solid solution between 55 and 65 per cent. antimony with a maximum on the liquidus curve at 63.5 per cent. antimony (1,018° C.) corresponding with the compound Fe_5Sb_4 .⁵ It is possible that the so-called compound Fe_3Sb_2 may not be a separate chemical entity. The crystal structure of FeSb_2 is rhombic, with $a = 3.189 \text{ \AA}$, $b = 5.819 \text{ \AA}$ and $c = 6.520 \text{ \AA}$. The unit cell contains two molecules of FeSb_2 . It is claimed that some of these alloys are resistant to acids, particularly to hydrochloric acid.⁶

Antimony-Cobalt Alloys.⁷—Two compounds are formed, CoSb (M.pt. 1,190° C.) and CoSb_2 (decomposing at 900° C.), with eutectics at 39 per cent. antimony (M.pt. 1,090° C.) and at 99 per cent. antimony (M.pt. 620° C.). Antimony is soluble in cobalt to the extent of 13 per cent., and the alloys, within this range, are magnetic, losing their magnetism at temperatures varying from 1,132° C. for pure cobalt to 927° C. for the 13 per cent. antimony alloy.

Antimony-Nickel Alloys.⁸—Two compounds are formed, NiSb (M.pt. 1,160° C.) and Ni_5Sb_2 (M.pt. 1,170° C.), with eutectics at 3.2 per cent. nickel (M.pt. 612° C.), at 47 per cent. nickel (M.pt. 1,072° C.) and at 65 per cent. nickel (M.pt. 1,100° C.). There are three solid solutions: α , between 33 and 40 per cent. nickel, β , between 92 and 100 per cent. nickel above 380° C., and γ , between 67 and 100 per cent. nickel below 380° C. Magnetic alloys are found in the range 92 to 100 per cent. nickel below 330° C., the magnetic transformation taking place at that temperature. The compound Ni_5Sb_2 is formed from another compound Ni_4Sb at 677° C. Within the range 55 to 67 per cent. nickel, both compounds appear to be stable at ordinary temperatures.

¹ Dreifuss, *Zeitsch. Elektrochem.*, 1922, 28, 100, 224.

² Murakami and Hatta, *Science Reports Tohoku Imp. Univ.*, 1933, [1], 22, 88; Williams, *loc. cit.*; Wedekind, *Ber.*, 1907, 40, 1259.

³ Kurnakov and Konstantinov, *Zeitsch. anorg. Chem.*, 1908, 58, 1; Portevin, *Revue de Metallurgie*, 1911, 8, 312.

⁴ Hägg, *Nova Acta Regiae Soc. Sci. Upsaliensis*, 1929, [4], 7, No. 1.

⁵ Vogel and Dannöhl, *Arch. Eisenhüttenw.*, 1934-5, 8, 39.

⁶ Frischer, *French Patent*, 1931, 725448.

⁷ Lossev, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 375; Lewkonja, *Zeitsch. anorg. Chem.*, 1908, 59, 293.

⁸ Lossev, *Zeitsch. anorg. Chem.*, 1906, 49, 58; Vigouroux, *Compt. rend.*, 1908, 147, 976.

Antimony-Palladium Alloys.¹—Several compounds of these metals have been described, including PdSb_2 (decomposing at 680°C.), PdSb (M.pt. 799°C.), Pd_5Sb_3 , Pd_2Sb (decomposing at 830°C.) and Pd_3Sb (M.pt. $1,182^\circ \text{C.}$). The existence of the compound Pd_5Sb_3 has not, however, been confirmed. Eutectics are formed at 9.7 per cent. palladium (M.pt. 586°C.), at 55 per cent. palladium (M.pt. 734°C.) and at 77 per cent. palladium (M.pt. $1,070^\circ \text{C.}$). Solid solutions are formed of antimony in palladium (up to 15 per cent. antimony), and of antimony in the compound Pd_3Sb (between 68.5 and 72.5 per cent. palladium).

Antimony-Platinum Alloys.²—A number of intermetallic compounds of these two metals has been reported, but the existence of one only, PtSb_2 (M.pt. $1,225^\circ \text{C.}$), has been definitely confirmed. It is possible that two others exist, namely, Pt_4Sb and PtSb , with transition points at 670°C. and 660°C. , respectively; the compound Pt_5Sb_2 previously reported has not been confirmed. Two eutectics are formed, one containing a trace of platinum (M.pt. 630°C.), and the other containing 77 per cent. platinum (M.pt. 670°C.).

A number of ternary alloy systems containing antimony have been at least partially examined. Among them may be mentioned antimony-copper-silver,³ antimony-copper-cadmium,⁴ antimony-copper-tin,⁵ antimony-copper-lead,⁶ antimony-copper-bismuth,⁷ antimony-copper-iron,⁸ antimony-silver-cadmium,⁹ antimony-silver-zinc,¹⁰ antimony-zinc-lead,¹¹ antimony-zinc-bismuth,¹² antimony-magnesium-aluminium,¹³ and antimony-tin-lead.¹⁴ The last-mentioned system includes the industrial alloys known as type-metals.¹⁵

¹ Sander, *Zeitsch. anorg. Chem.*, 1912, 75, 97; Grigoriev, *Ann. Inst. Platine*, 1929, 7, 32; *Zeitsch. anorg. Chem.*, 1932, 209, 308.

² Nemilov and Voronov, *Ann. Inst. Platine*, 1935, 12, 17; Friedrich and Leroux, *Metallurgie*, 1909, 6, 1.

³ Guertler and Rosenthall, *Zeitsch. Metallkunde*, 1932, 24, 7, 30.

⁴ Slicher, *Intern. Zeitsch. Metallographie*, 1913, 3, 102.

⁵ Tasaki, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1929, 12 A, 227.

⁶ Schack, *Zeitsch. anorg. Chem.*, 1923, 132, 265.

⁷ Parravano and Viviani, *Atti R. Accad. Lincei*, 1910, [5], 19, i, 835.

⁸ Vogel and Dannöhl, *Arch. Eisenhüttenw.*, 1934-5, 8, 83.

⁹ Guertler and Rosenthall, *loc. cit.*

¹⁰ Guertler and Rosenthall, *loc. cit.*

¹¹ Tammann and Dahl, *Zeitsch. anorg. Chem.*, 1925, 144, 1.

¹² Kremann, Langsbauer and Rauch, *Zeitsch. anorg. Chem.*, 1923, 127, 229.

¹³ Loofs-Rassow, *Hauszeit V.A.W. Erftwerk A.G. Aluminium*, 1931, 3, 20; Guertler and Bergmann, *Zeitsch. Metallkunde*, 1933, 25, 81, 111.

¹⁴ Iwasi and Aoki, *Kinzoku-no-Kenkyu*, 1931, 8, 253; Aoki and Waki, *Nackaku Insatsu-kyoku Kenyujo Chosa Hokoku*, 1930, No. 21, 1, 37, 47.

¹⁵ See also Wehenhoff, "Report of Technical Director, U.S. Govt. Printing Office"; "Appendix to Ann. Report of Public Printer," 1930, 105; Hertel and Demmer, *Metallwirtschaft*, 1931, 10, No. 7, 125; Weaver, *J. Inst. Metals*, 1935, 56, 209.

CHAPTER II.

COMPOUNDS OF ANTIMONY.

General.—The compounds of antimony conform, in general, to the types expected from the position of the metal in the Periodic Classification. Antimony exhibits two valencies only, being trivalent in some compounds and quinquevalent in others. Several substances, such as the suboxide, in which antimony shows an apparent valency of less than three, have been described ; but either these have been shown not to be true compounds, or their constitutions have not been fully elucidated. In accordance with its position in the Periodic Table, antimony shows electropositive properties more definitely than arsenic, forming true salts such as the halides and the sulphate; the salts, however, undergo hydrolysis, producing ultimately oxides or hydrated oxides. As might be expected, hydrolysis does not take place so readily, or proceed so completely, as with the compounds of arsenic, and several stable intermediate products are formed.

Antimony, like arsenic, forms a hydride ; stibine, however, can only be formed by the evolution method in acid solutions. It is more easily decomposed by heat than arsine.

Antimony halides are characteristic. There are two fluorides, the trifluoride and the pentafluoride, both of which are soluble in water and hydrolysed only slowly. Antimony trifluoride is not hydrolysed below 30° C. The corresponding chlorides hydrolyse more rapidly, the trichloride yielding oxychlorides, and ultimately (by hydrolysis at 150° C.) trioxide, and the pentachloride yielding hydrated antimony pentoxide (the so-called antimonic acid). Antimony pentachloride dissociates on heating. A third chloride, antimony tetrachloride, appears to exist in complex compounds only ; it has not been isolated. Antimony tribromide is the only bromide that has as yet been isolated. The pentabromide is unknown, but compounds have been obtained that may be regarded as derived from it. It is also possible that compounds of a hypothetical antimony tetrabromide may exist. Antimony tribromide is very readily hydrolysed. The only iodide known is the triiodide, a well-defined salt which readily hydrolyses. Complex compounds of quinquevalent antimony which contain fluorine and iodine have, however, been prepared.

The halides of antimony readily form double compounds, particularly with the halides of alkali and alkaline earth metals. In many cases there is definite evidence of the formation of complex anions of which antimony forms a constituent. Thus compounds are derived from antimony pentachloride which may be regarded as salts of ortho-, pyro- and meta-chloroantimonic acids, H_3SbCl_8 , H_2SbCl_7 , and HSbCl_6 . Of these acids meta-chloroantimonic acid has alone been isolated. From

antimony tribromide, salts of the type $M_2Sb_3Br_{11}$ have been prepared, in which M represents a monovalent metal. From antimony pentabromide salts of the bromantimonic acids have been obtained, and metabromantimonic acid, $HSbBr_6 \cdot 3H_2O$, has been isolated. Many other complex compounds of antimony halides have been prepared, the constitutions of which have not been fully elucidated. Most of them are decomposed by water, frequently with hydrolysis.

The chlorides and bromides of antimony are soluble in many organic solvents, and in many cases complexes are formed.¹

Three oxides are known. Of these, antimony trioxide is amphoteric, forming both antimony salts and antimonites; its basic properties, however, predominate. Antimony tetroxide is neutral or only faintly acidic, and may best be considered as a salt, antimony antimonate, $SbSbO_4$. Antimony pentoxide is acidic, forming antimonates. It is doubtful, however, if a true antimonic acid has been isolated, antimony resembling tin in this respect.

The heats of formation of the oxides are :

Antimony trioxide	163,000 calories
Antimony tetroxide	209,800 "
Antimony pentoxide	229,600 "

Of the compounds in which antimony is a constituent of the anion, antimonites are known, principally in the form of meta-antimonites, such as sodium meta-antimonite, $NaSbO_2$. Ortho- and pyro-antimonites may exist, but the latter in particular are doubtful. The free acids have not been isolated.

Meta-hypoantimonic acid, $H_2Sb_2O_5$, and its salts, derived from Sb_2O_4 , are known. They may be regarded as mixed antimonites and antimonates.

Ortho- and meta-antimonates are known, the majority of the salts being either acid ortho-antimonates of the type KH_2SbO_4 , or meta-antimonates of the type $KSbO_3$. It has also been suggested that the formula for antimonic acid is $HSb(OH)_6$.

It may also be noted that antimony pentoxide does not liberate chlorine from hydrochloric acid; it will, however, liberate iodine from hydriodic acid.

Three sulphides of antimony are known, corresponding to the three oxides; but the pentasulphide is very difficult to prepare in the pure state, most of the preparations formerly regarded as antimony pentasulphide being mixtures, probably of antimony tetrasulphide and sulphur. The presence of trivalent antimony can usually be shown in such preparations. Complex sulphur compounds, notably with the halides, are also known. They correspond roughly with the oxyhalides.

Of the other inorganic compounds of antimony, the sulphate and the nitrate have been reported, but both are more readily obtained as basic salts. The existence of the latter is somewhat doubtful. It is interesting to note, however, that antimony selenate is insoluble in water and is not decomposed by it.

Physiological Action of Antimony and its Compounds.—In the seventeenth and eighteenth centuries many medicinal preparations containing antimony were in vogue, but the utility of most of these is extremely doubtful. In the days of antiquity, antimonial wine was

¹ See this Series, Vol. XI, Part III.

frequently employed as an emetic. The use of antimonial preparations in medicine declined steadily, however, until comparatively recent years, when their applicability to the treatment of certain tropical and allied diseases was discovered.

In many ways the physiological action of antimony resembles that of arsenic, but the former element differs principally in that it is absorbed less easily and has a more irritating effect upon the alimentary canal.

The principal compound employed is tartar emetic, potassium antimonyl tartrate, $K(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$, but oxides and sulphides have also been used. Many organic compounds have been prepared; they have a more powerful effect than tartar emetic, but they are more toxic and are difficult to administer.

The action of antimony is principally that of an emetic; it appears to act by producing local irritation of the stomach, but its mode of action is not confined to this, since vomiting is also produced by intravenous or subcutaneous injections. It is, however, dangerous to use, as the consequent severe depression may lead to collapse. Antimony compounds also produce expectoration and perspiration.

When introduced into the stomach, antimony is slowly liberated from the compound in the form of tervalent ion, and this, in the presence of acids, produces the observed effects. When used in ointments antimony produces an irritation of the skin; this also is probably due to liberation of tervalent antimony ion.

Stibine is very poisonous, but although its effects appear to resemble those of arsine, its action is largely unknown.

Antimony trichloride has a caustic action, and combines with albumen in the same way as compounds of the heavy metals.

In recent years antimony has been found to exert a remarkable poisoning effect on trypanosomes and certain other protozoa. This has led to its recommendation, in the form of injections, in the treatment of certain tropical and allied diseases.¹

Antimonial poisoning has been diagnosed in many cases, instances having been found in connection with the enamel and printing trades.² Legislation has been introduced in some countries regulating the use of antimony in enamels, in which it acts as an opacifier. Criminal cases are also known, the effects of doses of antimony given at intervals frequently being mistaken for symptoms of disease. Antimony is, as a rule, found only in traces in the stomach after antimonial poisoning, the greater part being expelled by vomiting.

It is thought that antimony in the quinquivalent condition is comparatively non-poisonous.³

ANTIMONY AND HYDROGEN.

The only compound of antimony with hydrogen that is known with certainty is the gaseous antimony trihydride, or stibine, SbH_3 . A solid

¹ Cushny, "A Text-Book of Pharmacology and Therapeutics" (London, 1928, 9th Ed.), p. 676; Dixon, "A Manual of Pharmacology" (London, 1929, 7th Ed., p. 383; Uhlenhuth, *Klin. Wochschr.*, 1931, 10, 1153, 1201; Uhlenhuth and Seiffert, *Zentr. Bakt. Parasitenk.*, 1931, 122, 51; Myers and Throne, *J. Lab. Clin. Med.*, 1930, 16, 239; Schmidt, *Zeitsch. angew. Chem.*, 1930, 43, 963; van Hoek, *Farben Zeit.*, 1932, 37, 1749; 38, 43; Dyson, *Pharm. J.*, 1928, [4], 67, 596.

² Oliver, *Brit. Med. J.*, 1933, I, 1094; Ministry of Health (London), 1933, Memo. 171 (Med.).

³ Blyth and Blyth, "Poisons, Their Effects and Detection" (London, 1906, 4th Ed.), p. 606; Leschke, *Münch. med. Wochschr.*, 1932, 79, 57, 140; Melzer, *Glashütte*, 1929, 59, 865.

substance, described as **di-antimony dihydride**, Sb_2H_2 , is stated to have been obtained by various electrolytic methods and by the reduction of antimony compounds by nascent hydrogen.¹ It is a brownish-black substance, soluble in fairly concentrated nitric acid, but not in other mineral acids; it is insoluble in solutions of caustic alkalis. It is decomposed when heated in a current of hydrogen, and reacts vigorously with fused potassium nitrate.² On the other hand, this substance may be merely metallic antimony in a fine state of division, containing a trace of adsorbed hydrogen.³ Some investigators doubt the existence of a solid antimony hydride.⁴

Antimony Trihydride, or *Stibine*, SbH_3 .—This was first obtained in 1837.⁵ It may be prepared by the action of nascent hydrogen upon a solution of an antimony salt, the gas obtained being mixed with a large excess of hydrogen.⁶ The reaction is most conveniently carried out by the addition to a solution of an antimony salt of metallic zinc or aluminium and a mineral acid. When iron is used no antimony trihydride appears to be formed;⁷ with tin the yield is very small. If the reaction is carried out in alkaline solution, no hydride is formed.⁸ In this manner antimony trihydride differs from the corresponding hydride of arsenic.

Antimony trihydride may also be prepared by the action of dilute mineral acids upon alloys of antimony, convenient alloys being those of antimony with zinc,⁹ magnesium,¹⁰ sodium amalgam,¹¹ potassium¹² and calcium. If, however, the alloys of antimony and calcium are chemically pure, no hydride is obtained.¹³ Alloys with strontium and barium act less readily. Alloys of antimony and lead may be used with concentrated hydrochloric acid¹⁴ or hydrobromic acid.¹⁵ Alloys of antimony with lithium,¹⁶ aluminium, thallium and iron are unsuitable. The most satisfactory results are obtained with alloys of zinc or magnesium. The

¹ Weekes and Druce, *Rec. Trav. chim.*, 1925, 44, 970; *J. Chem. Soc.*, 1925, 127, 1069; Druce, *Chem. Listy*, 1925, 19, 156; Humpert, *J. prakt. Chem.*, 1865, 94, 398; Wiederhold, *Pogg. Annalen*, 1864, 122, 481; Marchand, *J. prakt. Chem.*, 1845, 34, 381; Ruhland, *Schweigger's J.*, 1815, 15, 418.

² Weekes and Druce, *J. Chem. Soc.*, 1925, 127, 1069.

³ Grant, *J. Chem. Soc.*, 1928, 131, 1987; Sand, Grant and Lloyd, *ibid.*, 1927, 130, 393.

⁴ Reckleben and Scheiber, *Zeitsch. anorg. Chem.*, 1911, 70, 275; Stock and Guttman, *Ber.*, 1904, 37, 885; Böttger, *J. prakt. Chem.*, 1856, 68, 374; *Pogg. Annalen*, 1856, 97, 333; 1858, 104, 292.

⁵ Thompson, *Phil. Mag.*, 1837, 10, 353; *J. prakt. Chem.*, 1837, 11, 369; Pfaff, *Pogg. Annalen*, 1837, 42, 339.

⁶ Seubert and Schmidt, *Annalen*, 1892, 267, 237; Thiele, *ibid.*, 1891, 265, 62; Fluckiger, *Arch. Pharm.*, 1889, [3], 27, 27; Böttger, *Jahresber.*, 1880, 1279; Skey, *Chem. News*, 1876, 34, 147; Roussin, *Zeitsch. anal. Chem.*, 1867, 6, 100; *J. Pharm. Chim.*, 1866, [4], 3, 413; Böttger, *J. prakt. Chem.*, 1856, 68, 374; Fleitmann, *Annalen*, 1851, 77, 126; Jacquelin, *Compt. rend.*, 1843, 16, 30; Vogel, *J. prakt. Chem.*, 1838, 13, 57; Simon, *Pogg. Annalen*, 1837, 42, 563; Thompson, *loc. cit.*; Pfaff, *loc. cit.*

⁷ Dupasquier, *Compt. rend.*, 1842, 14, 514; Thiele, *loc. cit.*

⁸ Fleitmann, *loc. cit.*; Gatehouse, *Chem. News*, 1872, 27, 189; Hager, *Zeitsch. anal. Chem.*, 1872, 11, 82.

⁹ Stock and Dohrt, *Ber.*, 1901, 34, 2339; 1902, 35, 2270; Bartels, *Inaugural Dissertation*, Berlin, 1899; Berthelot and Petit, *Ann. Chim. Phys.*, 1889, [6], 18, 65; Olszewski, *Monatsh.*, 1886, 7, 373; Lassaigne, *J. Chim. médicale*, Paris, 1840, [2], 6, 638; 1841, [2], 7, 440; Capitaine, *J. Pharm. Chim.*, 1839, [2], 25, 516; Vogel, *loc. cit.*; Thompson, *loc. cit.*

¹⁰ Stock and Dohrt, *loc. cit.*; Humpert, *J. prakt. Chem.*, 1865, 94, 398.

¹¹ van Bylert, *Ber.*, 1890, 23, 2968; Poleck and Thümmel, *Ber.*, 1883, 16, 2444.

¹² Schiel, *Annalen*, 1857, 104, 223.

¹³ Moissan, *Compt. rend.*, 1898, 127, 584.

¹⁴ von der Planitz, *Ber.*, 1874, 7, 1664.

¹⁵ Harding, *ibid.*, 1881, 14, 2092.

¹⁶ Lebeau, *Compt. rend.*, 1902, 134, 284.

state of division of the alloy, and the temperature at which the reaction takes place, greatly influence the yield, the best results being obtained by allowing small portions of finely-divided alloy to fall gradually into cold dilute, oxygen-free hydrochloric acid.

Attempts have been made to prepare antimony trihydride by electrolytic processes. Newbury found appreciable quantities of this gas in the hydrogen liberated from an antimony cathode in acid solution.¹ Later investigations have been carried out using both acid and alkaline solutions. No stibine is produced at low concentrations, while with increasing concentrations the gas is decomposed almost as soon as it is formed, particularly in alkaline solutions. The yield decreases with rise of temperature.² The electrolytic formation of stibine has been studied quantitatively, and equations have been adduced correlating the percentage yield of stibine at an antimony electrode in solutions of caustic alkali with temperature, with hydrogen-ion concentration, and with the voltage between a hydrogen electrode immersed in the experimental solution and a saturated calomel electrode;³ similar equations for solutions of sodium carbonate or sodium sulphate have also been obtained. In acid solutions, however, stibine is formed only with difficulty, the required current density being sufficiently high to cause elevation of the temperature of the electrolyte to an inhibitive degree.⁴ Alkaline solutions appear to be more favourable to stibine formation, but it is necessary to remove rapidly any stibine produced by blowing a current of hydrogen past the electrode; failing this the stibine is at once decomposed with precipitation of metallic antimony. It has also been suggested that, although the electrolytic method of preparation is not practical, the best conditions are obtained by using a concentrated aqueous solution of sodium acetate containing acetic acid, with an antimony cathode.⁵ The best yield is obtained with a current density of 14 amps. per sq. dm., increase in current increasing the yield and increase in voltage diminishing it.

The gas is most conveniently dried by passing over calcium chloride or phosphorus pentoxide, then collecting over mercury; other desiccating agents cause decomposition.⁶ It may be separated from hydrogen by liquefaction.

Antimony trihydride is a colourless gas with a very characteristic smell, described as faintly resembling that of hydrogen sulphide;⁷ its taste is extremely unpleasant,⁸ and it is very poisonous. Its vapour density at 15° C. and 754 mm. is 4.86 (air=1),⁹ in agreement with the formula SbH_3 . It shows appreciable deviation from the gas laws.¹⁰ When cooled in liquid ethylene it solidifies to a snow-white mass, crystals being formed in liquid air.¹¹ The solid melts at -88° C., forming a colourless liquid which boils at -17° C. The density of the liquid is

¹ Newberry, *J. Chem. Soc.*, 1916, 109, 1361; Paneth, *Zeitsch. Elektrochem.*, 1920, 26, 453.

² Sand, Weekes and Worrell, *J. Chem. Soc.*, 1923, 123, 456.

³ Weekes, *Rec. Trav. chim.*, 1924, 43, 649; 1925, 44, 201, 795.

⁴ Sand, Grant and Lloyd, *J. Chem. Soc.*, 1927, 130, 389.

⁵ Hlasko and Maslowski, *Roczniki Chem.*, 1930, 10, 240.

⁶ Stock and Guttman, *Ber.*, 1904, 37, 885; Brunn, *Ber.*, 1889, 22, 3205.

⁷ Stock and Dohrt, *Ber.*, 1901, 34, 2339.

⁸ Jones, *J. Chem. Soc.*, 1876, 29, 641.

⁹ Stock and Guttman, *loc. cit.*

¹⁰ Stock, Echeandia and Voigt, *Ber.*, 1908, 41, 1309.

¹¹ Olszewski, *Monatsh.*, 1886, 7, 373; Stock and Dohrt, *Ber.*, 1902, 35, 2270.

2.26 at -25° C. and 2.34 at -50° C.¹ The gas is slightly soluble in water (to the extent of 0.2 volume in 1 volume of water); the solution in water free from air is fairly stable. It is more soluble in alcohol (15 volumes in 1) and is very soluble in carbon disulphide (250 volumes in 1). It is also fairly soluble in other organic solvents, but such solutions are in general less stable than aqueous solutions.²

In its physiological effects the gas strongly resembles arsenic trihydride; exposure to an atmosphere containing 1 per cent. is fatal to mice in a few seconds.³ Although opinions as to the physiological effect of stibine are conflicting, especially among the earlier workers, it is probable that its action upon human blood is similar to that of arsine, in that the oxyhæmoglobin is reduced.⁴

Antimony trihydride is an endothermic compound; the heat of formation, determined by decomposing the gas into its elements by means of the electric spark, is $-33,980$ gram-calories at constant pressure, and $-34,270$ gram-calories at constant volume.⁵ From an investigation of the electrolytic formation of stibine, the free energy of the reaction $2\text{Sb} + 3\text{H}_2 = 2\text{SbH}_3$ has been calculated to be $62,100$ gram-calories for two moles of the gas in an acid solution, and $62,000$ gram-calories for two moles in an alkaline solution.⁶

Stibine is readily decomposed into its elements; if the gas is pure and dry, however, it remains fairly stable when kept in a thoroughly clean glass vessel. Air and aerated water produce some decomposition, but water free from air appears to be without action.⁷ Decomposition does not appear to be caused by light.⁸ The velocity of the decomposition depends considerably upon the nature of the surface in contact with the gas, an etched surface, or one coated with an antimony mirror, acting catalytically. The presence of hydrogen does not affect the rate of decomposition; oxygen poisons the antimony mirror which, however, recovers its activity after some hours. It is probable that the effect of oxygen is to oxidise the hydride, not the mirror itself. The rate of decomposition is also affected by the nature of the surface of the antimony mirror.⁹

By the action of heat alone stibine is decomposed more readily than arsine, rapid decomposition occurring at temperatures above 150° C. If the reaction is carried out in a clean glass tube heated locally, an antimony mirror is deposited on both sides of the heated part; this reaction is employed in the well-known Marsh's test.¹⁰

Liquid stibine is partially decomposed even at low temperatures, decomposition beginning between -65° C. and -56° C. Decomposition takes place more rapidly in the liquid than in the gaseous state,

¹ Stock and Guttman, *loc. cit.*

² Stock and Guttman, *loc. cit.*

³ Stock and Guttman, *loc. cit.*

⁴ Joly and de Nabais, *Compt. rend.*, 1890, 110, 667; Stock, Guttman and Bergell, *Ber.*, 1904, 37, 893; Jones, *J. Chem. Soc.*, 1876, 29, 641.

⁵ Stock and Wrede, *Ber.*, 1908, 41, 540.

⁶ Sand, Weekes and Worrall, *J. Chem. Soc.*, 1923, 123, 456. See also Berthelot and Petit, *Compt. rend.*, 1889, 108, 546.

⁷ Stock and Doht, *Ber.*, 1901, 34, 2343.

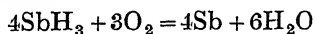
⁸ Lassaigue, *loc. cit.*; Stock and Doht, *loc. cit.*; Stock and Guttman, *loc. cit.*

⁹ Stock, Echeandia and Voigt, *Ber.*, 1908, 41, 1309; Stock, Gemolka and Heynemann, *ibid.*, 1907, 40, 532; Stock and Bodenstein, *ibid.*, 1907, 40, 570; Stock and Guttman, *ibid.*, 1904, 37, 901, 1957.

¹⁰ Brunn, *Ber.*, 1889, 22, 3202; Stock and Doht, *Ber.*, 1901, 34, 2273, 2343; van Bijlert, *Ber.*, 1890, 23, 2968; Böttger, *J. prakt. Chem.*, 1838, 13, 57.

but no evidence has been obtained of the formation of a lower hydride as one of the products of decomposition.¹

Stibine is oxidised by air or oxygen even at low temperatures according to the equation



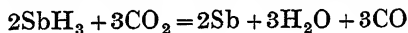
Under ordinary conditions black antimony is deposited, but at -90°C . the yellow modification is obtained. Liquid air does not cause oxidation. When burned in air, antimony trioxide is obtained instead of the metal.

Stibine is readily decomposed at the ordinary temperature by the halogens, forming antimony halides and halogen acids.²

Sulphur reacts slowly with a mixture of stibine and hydrogen heated to 100°C ., antimony trisulphide and hydrogen sulphide being formed; the action is accelerated by light.³ Pure stibine reacts readily with finely divided sulphur.⁴ Hydrogen sulphide appears to be without action at the ordinary temperature.⁵ When stibine is passed into concentrated sulphuric acid a black precipitate is obtained which is probably metallic antimony.⁶

Neither nitrogen nor ammonia reacts with stibine.⁷ The gas is oxidised by oxides of nitrogen⁸ and by nitric acid.⁹ Phosphorus trichloride has no action, while the pentachloride reacts only slowly.¹⁰ The iodides of phosphorus and the halides of antimony react with decomposition of the gas.¹¹

Stibine is oxidised when an electric spark is passed through a mixture of the gas with carbon dioxide, according to the equation: ¹²



Decomposition is also induced by the action of potassium hydroxide¹³ and other alkali and alkaline earth hydroxides.¹⁴

The action of stibine on a number of aqueous salt solutions has been studied.¹⁵ Stibine resembles arsine in its action on an aqueous solution of potassium permanganate.¹⁶ The precipitated manganese sesquioxide, Mn_2O_3 , is more flocculent when stibine is used, and the solution contains

¹ Stock and Guttman, *loc. cit.*; Olszewski, *loc. cit.*

² Stock and Guttman, *loc. cit.*; Brunn, *loc. cit.*; Husson, *Compt. rend.*, 1868, 67, 56; Vogel, *J. prakt. Chem.*, 1838, 13, 57; Buchner, *Repertorium Pharmacie*, Nürnberg, 1838, 63, 1838.

³ Jones, *loc. cit.*

⁴ Stock and Guttman, *loc. cit.*

⁵ Stock and Guttman, *loc. cit.*; see, however, Brunn, *loc. cit.*; Jones, *loc. cit.*

⁶ Humpert, *loc. cit.*; Bartels, *Inaugural Dissertation*, Berlin, 1889; Brunn, *loc. cit.* For the action of other sulphur compounds, see Jones, *loc. cit.*; Schiel, *Annalen*, 1857, 104, 223.

⁷ Simon, *loc. cit.*; Bartels, *loc. cit.*; Stock and Guttman, *loc. cit.*

⁸ Stock and Guttman, *loc. cit.*

⁹ Ansell, *J. Chem. Soc.*, 1852, 5, 210.

¹⁰ Mahn, *Jenaische Zeitsch.*, 1869, 5, 162.

¹¹ Stock and Guttman, *loc. cit.*

¹² Stock and Guttman, *loc. cit.*

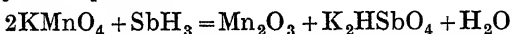
¹³ Bartels, *Inaug. Dissertation*, Berlin, 1899; Dragendorff, *Zeitsch. anal. Chem.*, 1866, 5, 200; Meissner and Hankel, *J. prakt. Chem.*, 1842, 25, 243.

¹⁴ Lionet, *Compt. rend.*, 1879, 89, 440.

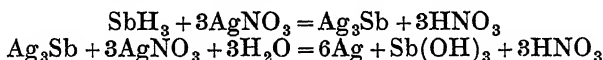
¹⁵ Bartels, *loc. cit.*; Dowzard, *J. Chem. Soc.*, 1901, 79, 715; Mahn, *loc. cit.*; Jacquelin, *Compt. rend.*, 1843, 16, 13.

¹⁶ Jones, *J. Chem. Soc.*, 1878, 33, 98. For the action with other oxidising agents, see Lemoult, *Compt. rend.*, 1904, 139, 478; Bartels, *loc. cit.*; Fluckiger, *Arch. Pharm.*, 1889, [3], 27, 26; *Zeitsch. anal. Chem.*, 1891, 30, 117; Varenne and Herbé, *Bull. Soc. chim.*, 1877, [2], 28, 523; *Zeitsch. anal. Chem.*, 1878, 17, 349; Schobig, *J. prakt. Chem.*, 1876, [2], 14, 291; *Bull. Soc. chim.*, 1877, [2], 28, 523; Mayençon and Bergeret, *Compt. rend.*, 1874, 79, 118.

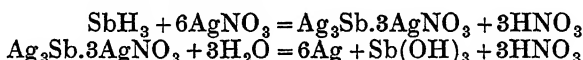
potassium antimonate and a trace of manganese. The reaction may be represented by the equation :



The reaction between stibine and an aqueous solution of silver nitrate has received considerable attention. The black precipitate that is formed was formerly ¹ thought to be silver antimonide, Ag_3Sb . The reaction was therefore thought to be different from that with arsine, but subsequent investigation has shown that the proportion of antimony in the precipitate does not correspond to that required by silver antimonide. It is now considered that the action of stibine closely resembles that of arsine, and may perhaps be represented by the equations :



The second reaction occurs with excess of silver nitrate.² The hydrated antimony oxide is almost completely insoluble in the resultant liquid and is thus precipitated with the silver. In this way the action differs from that of arsine. The precipitate is also stated to contain a little metallic antimony. The antimony oxide can be dissolved out of the precipitate by treatment with hot concentrated hydrochloric acid or with tartaric acid. By the action of stibine on a concentrated aqueous solution of silver nitrate a greenish-yellow coloration is obtained, but the substance producing this colour has not been isolated. It is suggested ³ that this compound may be $\text{Ag}_3\text{Sb} \cdot 3\text{AgNO}_3$, corresponding to the similar compounds of phosphorus and arsenic produced by the action of phosphine and arsine respectively on solutions of silver nitrate, and the suggestion is supported by the results of approximate analysis of the coloured mixture. On this assumption the action of stibine may be represented by the equations :



thus further emphasising the resemblance between phosphine, arsine and stibine. It has also been suggested that the greenish-yellow coloration may be due to the formation of the compound $\text{Ag}(\text{SbH}_3)\text{NO}_3$, analogous to $\text{Ag}(\text{NH}_3)\text{Cl}$, but there appears to be no confirmation of this.⁴ The reaction with silver nitrate has been suggested for the detection of traces of stibine.⁵

When stibine acts upon sodium aurichloride, a violet stain is produced ; similar stains are obtained with phosphine and arsine, but not with hydrogen. This reaction is suggested as a sensitive test for these hydrides. Organic matter must be destroyed prior to the test ; hydrogen sulphide also interferes.⁶

¹ Lassaigne, *J. Chim. méd.*, 1840, 17, 443.

² Reckleben and Güttich, *Zeitsch. anal. Chem.*, 1910, 49, 73; Reckleben, *Ber.*, 1909, 42, 1458; Güttich, *Inaug. Dissertation, Leipzig*, 1909; Vitali, *L'Orosi*, 1892, 397.

³ Poleck and Thümmel, *Ber.*, 1883, 16, 2435.

⁴ Bartels, *Inaug. Dissert.*, Berlin, 1889.

⁵ Weekes, *Chem. News*, 1923, 126, 275. For further literature, see Fresenius, "*Anleitung zur qualitativen chemischen Analyse*" (Braunschweig), 6th Ed., 1895, p. 248; Schobig, *loc. cit.*; Houzeau, *Compt. rend.*, 1872, 75, 1823; *Zeitsch. anal. Chem.*, 1873, 12, 312; Humpert, *J. prakt. Chem.*, 1865, 94, 398; Hofmann, *Annalen*, 1860, 115, 287; Simon, *ibid.*, 1837, 42, 563; Pfaff, *ibid.*, 1837, 42, 563.

⁶ Zimmermann, *Apotheker-Zeitung*, 1921, 36, 26.

The best absorbents for stibine are solutions of silver salts, iodine and iodic acid.¹

A number of organic substitution compounds of stibine have been prepared and described.² They are for the most part more stable than stibine itself.

ANTIMONY AND THE HALOGENS.

Antimony and Fluorine.

Two compounds of antimony and fluorine are known; antimony trifluoride, SbF_3 , and antimony pentafluoride, SbF_5 . Two other compounds have been reported,³ but it is probable that these are double compounds having the formulæ $\text{SbF}_5 \cdot 2\text{SbF}_3$ and $\text{SbF}_5 \cdot 3\text{SbF}_3$.

Antimony Trifluoride, SbF_3 , was first prepared by Berzelius in 1824 by evaporating a solution of antimony trioxide in hydrofluoric acid;⁴ Dumas prepared the same compound in 1826 by distilling a mixture of mercuric fluoride and powdered antimony.⁵ It has also been prepared by heating antimony trichloride with hydrofluoric acid in the presence of an organic solvent.⁶ Metallic antimony does not dissolve in concentrated hydrofluoric acid.⁷

Antimony trifluoride is most conveniently prepared by the method of Berzelius. Pure antimony trioxide is dissolved in excess of hydrofluoric acid, and the solution is evaporated until a film forms on the surface. On cooling, long, needle-shaped crystals separate out. These may be dried between filter-paper and stored in vessels of gutta-percha or platinum.⁸

Antimony trifluoride forms colourless, transparent, rhombic crystals of density⁹ (at 20.9°C.) 4.379. Its melting point is 292°C. or slightly lower;¹⁰ it sublimes when heated in a platinum vessel.¹¹ The solubility in water is as follows:

$t^\circ \text{C.}$	0	20	25	30
SbF_3 (grams per 100 grams water)	384.7	451.0	494.0	565.6

The solubility is increased by the presence of hydrofluoric acid and of alkali salts.¹²

The heat of formation of antimony trifluoride is 144,300 gram-calories.¹³ It does not fume in air, but when heated it volatilises with partial decomposition, leaving a residue of antimony trioxide. It is very hygroscopic. If an aqueous solution is evaporated without the addition of hydrofluoric acid, some antimonyl fluoride is obtained; no hydrolysis is apparent, however, below 30°C. ¹⁴

¹ Reckleben and Guttich, *loc. cit.*

² This Series, Vol. XI, Part III.

³ Ruff, Plato and Graf, *Ber.*, 1904, 37, 673.

⁴ Berzelius, *Pogg. Annalen*, 1824, i, 34.

⁵ Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 433.

⁶ Kinetic Chemicals, Inc., *French Patent*, 1931, 720589; *German Patent*, 1934, 602697.

⁷ Flückiger, *Pogg. Annalen*, 1852, 87, 249; *Annalen*, 1852, 84, 248; *Ann. Chim. Phys.*, 1853, [3], 39, 495.

⁸ Guntz, *Ann. Chim. Phys.*, 1884, [6], 3, 47. See also Rosenheim and Grünbaum, *Zeitsch. anorg. Chem.*, 1909, 61, 187.

⁹ Ruff, Plato and Graf, *Ber.*, 1904, 37, 673.

¹⁰ Carnelley, *J. Chem. Soc.*, 1878, 33, 275.

¹¹ Swartz, *Bull. Acad. roy. Belg.*, 1892, [3], 24, 310.

¹² Rosenheim and Grünbaum, *Zeitsch. anorg. Chem.*, 1909, 61, 187.

¹³ Guntz, *loc. cit.*; *Compt. rend.*, 1884, 98, 303, 512.

¹⁴ Rosenheim and Grünbaum, *loc. cit.*

Chlorine reacts with antimony trifluoride forming the compound 1
 $2\text{SbF}_5 \cdot \text{SbCl}_5$.

Liquid ammonia reacts with antimony trifluoride to form the
di-ammoniate, $\text{SbF}_3 \cdot 2\text{NH}_3$. This is a yellow powder which loses
 ammonia in the presence of moist air.²

Antimony trifluoride shows a tendency to form double and complex
 salts. From the thermochemical examination of solutions in hydro-
 fluoric acid, Guntz concluded that an acid fluoride is formed, but was
 unable to isolate it.³ Beck⁴ concluded that the most stable complex
 formation is of the type MSbF_4 or $\text{SbF}_3 \cdot \text{MF}$, in which the antimony is
 trivalent.

Numerous double compounds are formed with alkali fluorides, either
 by crystallisation from solutions of the mixed salts, or by addition of
 alkali carbonate to a solution of antimony trioxide in hydrofluoric acid.
 Salts in which the ratio $\text{SbF}_3 : \text{MF}$ has the following values have been
 obtained: 4 : 1, 3 : 1, 2 : 1, 7 : 4, 1 : 1, 1 : 2 and 1 : 3. They are colour-
 less, crystalline compounds and contain no combined water; they are
 fairly stable in air, and dissolve readily in water without producing
 turbidity; the solutions are acid, and attack glass. The salts can be
 regained from these solutions by evaporation.⁵

Double compounds with alkali chlorides and sulphates have also
 been obtained, having the general formulæ $\text{MCl} \cdot \text{SbF}_3$, $\text{M}_2\text{SO}_4 \cdot \text{SbF}_3$,
 $3\text{M}_2\text{SO}_4 \cdot 4\text{SbF}_3$ and $\text{M}_2\text{SO}_4 \cdot 2\text{SbF}_3$, where M represents a univalent
 metal. They may be prepared by the first method mentioned above,
 by the action of basic antimony sulphate on the corresponding fluoride,
 or by the action of alkali sulphate upon antimony trifluoride in the
 presence of hydrochloric acid.⁶ In general they crystallise fairly well,
 without combined water; they are fairly stable and not hygroscopic.
 Their solutions in water are strongly acid and attack glass.

Other double compounds have also been obtained. In some cases
 there is evidence for the existence of a complex ion in solution, but
 not in others. Solutions containing potassium nitrate, potassium
 sulphate or oxalic acid give no evidence of a complex ion; while
 solutions containing normal sodium oxalate or tartrate, ammonium
 oxalate or potassium antimonyl tartrate indicate decidedly the forma-
 tion of such ions. The following crystalline compounds have been
 obtained: ⁷ $3\text{KNO}_3 \cdot \text{SbF}_3$, $4(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{SbF}_3$, $2\text{Na}_2\text{C}_2\text{O}_4 \cdot 8\text{SbF}_3$ and
 $\text{K}_3\text{SbO}(\text{C}_2\text{O}_4)_2 \cdot \text{SbF}_3 \cdot 8\text{H}_2\text{O}$.

Salts containing antimony trifluoride have been used as mordants;
 but only those salts which yield complex ions in dilute solution are
 suitable for such purpose.⁸

¹ Ruff, Stauber and Graf, *Zeitsch. anorg. Chem.*, 1908, 58, 325.

² Ruff, etc., *Ber.*, 1906, 39, 4310.

³ Guntz, *Compt. rend.*, 1884, 98, 300. See also Redenz, *Arch. Pharm.*, 1898, 236, 265.

⁴ Beck, *Zeitsch. anorg. Chem.*, 1928, 174, 31.

⁵ Fluckiger, *loc. cit.*; von Raad and Hauser, *Ber.*, 1890, 23, Ref. 125; *German Patent*, 1888, 50381; Frölich, *Ber.*, 1891, 24, Ref. 170; *German Patent*, 1890, 53618; Ephraim and Heymann, *Ber.*, 1909, 42, 4456.

⁶ de Haën, *Ber.*, 1888, 21, Ref. 901; *German Patents*, 1887, 45222; 1887, 45224; Hasslacher, *Ber.*, 1892, 25, Ref. 231; *German Patent*, 1890, 57615; Mayer, *Ber.*, 1894, 27, Ref. 922; *German Patent*, 1892, 76168; von Raad, *Ber.*, 1896, 29, Ref. 321; *German Patent*, 1894, 85626.

⁷ Rosenheim and Grünbaum, *loc. cit.* See also Frölich, *Ber.*, 1896, 29, Ref. 447; *German Patent*, 1894, 86668.

⁸ Rosenheim and Grünbaum, *loc. cit.*

Antimony Pentafluoride, SbF_5 , was first reported by Berzelius in 1824, who obtained it by the action of hydrofluoric acid on antimonic acid; ¹ for some time the existence of this compound was denied, ² until in 1867 Marignac confirmed the results of Berzelius, including the preparation of a number of double compounds. ³ In 1891 Moissan prepared the compound by direct union of the elements. ⁴

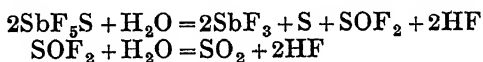
Antimony pentafluoride is most conveniently prepared either by the method of Berzelius or by the action of anhydrous hydrogen fluoride upon antimony pentachloride. ⁵ The latter method is carried out by heating a mixture of hydrogen fluoride and antimony pentachloride at 25° to 30° C. until no more hydrochloric acid is evolved; after a considerable time the boiling point of the mixture rises to 150° to 155° C., at which temperature antimony pentafluoride distils over.

The pentafluoride is a colourless, thick, oily liquid which boils at 149° to 150° C. Its density at 22.7° C. is 2.993. It is soluble in water and is hygroscopic. It has a drastic action upon the skin. ⁶

The *dihydrate*, $\text{SbF}_5 \cdot 2\text{H}_2\text{O}$, has also been prepared.

Chlorine appears to have no action upon antimony pentafluoride; bromine reacts to form a viscid, dark brown mass of indefinite composition, which may contain the compound SbF_5Br . Iodine forms two compounds. With excess of antimony pentafluoride at 160° to 220° C. a dark, bluish-green substance, $(\text{SbF}_5)_2\text{I}$, is formed, melting at 110° to 115° C. It does not lose iodine when heated to 240° C., but it is readily decomposed by water. When antimony pentafluoride is heated with excess of iodine at a temperature above the boiling point of iodine, a dark brown compound, SbF_5I , is formed, melting at 80° C. This compound is decomposed when heated above 260° C. with evolution of iodine, but it is not so readily decomposed by water as the former compound.

Sulphur dissolves in antimony pentafluoride to form a dark blue solution from which the compound SbF_5S can be separated. This melts at 230° C., is very hygroscopic, and is decomposed by water and moist air. The decomposition by water is probably represented by the equations:



Antimony pentafluoride is decomposed when a current of hydrogen sulphide is passed over it, the products being sulphur, hydrogen fluoride and antimony thio-fluoride. An aqueous solution reacts with hydrogen sulphide only when it is warmed.

The pentafluoride reacts with nitrogen sulphide, sulphur dichloride and chromyl chloride; also with molybdenum pentachloride and tungsten hexachloride forming respectively a molybdenum fluoride and tungsten hexafluoride, together with double compounds with antimony pentafluoride.

When dry ammonia is passed over the pentafluoride the latter

¹ Berzelius, *loc. cit.*

² Flückiger, *Annalen*, 1852, 84, 248.

³ Marignac, *Bull. Soc. chim.*, 1867, [2], 8, 323; *Ann. Chim. Phys.*, 1867, [4], 10, 371; *Annalen*, 1868, 145, 239.

⁴ Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 247.

⁵ Ruff, Plato and Graf, *Ber.*, 1904, 37, 673; Ruff, Graf, Heller and Knoch, *Ber.*, 1906, 39, 4310.

⁶ For a discussion of the space chemistry of this compound, see Ruff, Ebert and Menzel, *Zeitsch. anorg. Chem.*, 1932, 207, 46.

becomes coated with a yellowish-red crust of indefinite composition ; the action is vigorous until the protective coat is formed, which then prevents further action. When heated with liquid ammonia at 100° C. in a platinum tube a white powder is formed which is probably the complex substance $\text{NH}(\text{SbF}_3 \cdot \text{NH}_3 \cdot \text{HF})_2$. It is readily decomposed by moist air ; its solution is acid towards litmus and it is slowly acted upon by water with the formation of antimonious acid.

Antimony pentafluoride reacts with phosphorus forming a yellow vapour, with phosphorus trichloride forming phosphorus trifluoride, and with phosphorus pentoxide forming phosphorus oxyfluoride.¹

With arsenic trifluoride a series of crystalline compounds is formed ; and with antimony trifluoride, a series of compounds ranging from $\text{SbF}_5 \cdot 2\text{SbF}_3$ to $\text{SbF}_5 \cdot 5\text{SbF}_3$. These may be prepared by distilling a mixture of antimony pentafluoride and antimony trifluoride. The compound $\text{SbF}_5 \cdot 2\text{SbF}_3$ is a colourless, transparent, crystalline substance ; its density at 21° C. is 4.188 ; it boils at 390° C. and it is hygroscopic. The compound $\text{SbF}_5 \cdot 5\text{SbF}_3$ boils at about 384° C.²

Antimony pentafluoride reacts with the tetrachlorides of tin, titanium and silicon with evolution of hydrogen chloride in each case. When warmed with colloidal silicic acid, antimonious acid and silicon tetrafluoride are formed.

Many carbonaceous materials are attacked by the pentafluoride, including filter-paper, cork, wood, india-rubber, benzene, ether, alcohol, acetone, glacial acetic acid, ethyl acetate, carbon disulphide, light petroleum and chloroform. With chloroform an easily liquefiable gas (probably CCl_3F) is formed.

Antimony pentafluoride when dry does not react with the majority of metals. When heated with sodium a violent reaction occurs and a white vapour is formed. It is reduced to the trifluoride when heated with powdered antimony.

The pentafluoride can be converted quantitatively into sodium hydrogen pyroantimonate by the addition of sodium hydroxide or sodium carbonate.³

A double compound of antimony pentafluoride and antimony pentachloride, $2\text{SbF}_5 \cdot \text{SbCl}_5$, is obtained by the action of chlorine on antimony trifluoride.⁴ Several other double compounds of these two pentahalides are indicated by the results of an investigation of the freezing point curves of mixtures of the two.⁵ Four of these compounds have been isolated : $2\text{SbF}_5 \cdot \text{SbCl}_5$ (D_4^{20} 3.08), $\text{SbF}_5 \cdot \text{SbCl}_5$, $2\text{SbF}_5 \cdot 3\text{SbCl}_5$ (D_4^{20} 2.79), and $\text{SbF}_5 \cdot 3\text{SbCl}_5$ (D_4^{20} 2.73) ; two other compounds, $3\text{SbF}_5 \cdot \text{SbCl}_5$ and $\text{SbF}_5 \cdot 2\text{SbCl}_5$, are also believed to exist. They are all decomposed on fusion. Molecular weight determinations have been made in solutions in sulphuryl chloride : the compounds $2\text{SbF}_5 \cdot 3\text{SbCl}_5$ and $\text{SbF}_5 \cdot 3\text{SbCl}_5$ give values which are only about one-third of the theoretical molecular weight, while the compound $2\text{SbF}_5 \cdot \text{SbCl}_5$ does not appear to dissociate in 10 per cent. or more concentrated solution. The molecular volumes of some of these compounds indicate that there is a considerable decrease in volume when the compounds are formed from

¹ Ruff, Graf, Heller and Knoch, *loc. cit.*

² Ruff, Plato and Graf, *loc. cit.*

³ Ruff, Graf, Heller and Knoch, *loc. cit.*

⁴ Ruff, Stäuber and Graf, *Zeitsch. anorg. Chem.*, 1908, 58, 325.

⁵ Ruff, Zedner, Knoch and Graf, *Ber.*, 1909, 42, 4021.

their constituents. Chemically the compounds closely resemble corresponding mixtures of the two binary compounds. Bromine reacts with all of them. When the compound $2\text{SbF}_5 \cdot \text{SbCl}_5$ is mixed with nitrosyl fluoride at -80°C ., and the mixture allowed to warm up, the compound $\text{SbF}_5 \cdot \text{NOF}$ is obtained as slender, colourless, needle-shaped crystals. This compound may also be obtained by the action of nitrosyl fluoride on antimony pentafluoride, and by the action of antimony pentafluoride on the corresponding arsenic compound, $\text{AsF}_5 \cdot \text{NOF}$. The compound $\text{SbF}_5 \cdot \text{NOF}$ sublimes below red heat without decomposition; it is very hygroscopic and is decomposed by water and by alcohol. It reacts with potassium fluoride with the formation of a double compound of potassium fluoride and antimony pentafluoride and separation of nitrosyl fluoride.¹

Antimony pentafluoride forms a number of double compounds with alkali chlorides and fluorides of the general type $\text{SbF}_5 \cdot \text{MF}$ and $\text{SbF}_5 \cdot 2\text{MF}$. These may be prepared by the addition of alkali hydroxide to an acid solution of antimony pentafluoride, or by the solution of alkali antimonate in hydrofluoric acid. They are all deliquescent and soluble in water, but are stable when dry. Their solutions in water evolve hydrogen fluoride, and on evaporation yield oxyfluorides. The solutions will react with hydrogen sulphide only after prolonged treatment.

Certain compounds of antimony pentafluoride with organic bases have also been obtained.²

Antimony and Chlorine.

Two chlorides of antimony, namely the trichloride and pentachloride, are known with certainty; the tetrachloride has also been reported.

Antimony Trichloride, SbCl_3 , has been known for a long time, having been prepared by Basil Valentine by distilling a mixture of antimony trisulphide and mercuric chloride; it was at one time thought that the substance was a compound of mercury, but Glauber disproved this in 1648. That the trichloride is decomposed by water was known to Basil Valentine, while the oxychloride produced was called by Paracelsus *mercurius vitae*, in the belief that it was related to mercury. At the end of the sixteenth century the trichloride (probably admixed with oxychloride) was introduced into medicinal preparations by Victor Algarotus of Verona, under the name of *pulvis angelicus*.³

Antimony trichloride is most conveniently prepared by the action of concentrated hydrochloric acid upon antimony trisulphide; when all the hydrogen sulphide has been evolved, the residue is distilled; after rejecting the first distillate, which contains most of the volatile impurities, the final distillate is collected as a white, pasty mass of antimony trichloride.⁴

¹ Ruff, Stäuber and Graf, *loc. cit.*

² Berzelius, *loc. cit.*; Marignac, *loc. cit.*; Redenz, *Arch. Pharm.*, 1898, 236, 267.

³ Basilius Valentinus, "*The Triumphant Chariot of Antimony*," English Translation, London, 1661; Glauber, *Opera chymica* (Frankfurt am Main), 1658, English Translation (London), 1689; see also Dyson, *Pharmaceutical Journal and Pharmacist*, 1928, [4], 67, 397.

⁴ Lang and Carson, *J. Soc. Chem. Ind.*, 1902, 21, 1018; Warren, *Chem. News*, 1892, 65, 232; Tooke, *J. Chem. Soc.*, 1862, 15, 462; Larocque, *J. Pharm. Chim.*, 1849, [3], 15, 161; Geiger and Reimann, *Magazin der Pharmacie*, 1827, 17, 126; Göbel, *Archiv Apothekervereins*, 1822, [2], 216; Brandes, *Repertorium Pharmacie*, 1821, 11, 289; Rolfink, *Crell's Chemisches Journal*, 1781, [6], 76; de Koninck and Leorenier, *Zeitsch. anal. Chem.*, 1888, 27, 462; Lang, *Ber.*, 1885, 18, 2714.

Numerous chemical reactions resulting in the formation of antimony trichloride have been described. It may be obtained from metallic antimony by the action of chlorine,¹ acid chlorides,² magnesium chloride³ and other metallic chlorides.⁴ Hydrochloric acid, free from air, does not attack antimony, but in the presence of air, antimony trichloride is formed slowly; the action is accelerated by the presence of a little nitric acid.⁵

Antimony trioxide is converted into the trichloride by the action of chlorine,⁶ chlorides of non-metals⁷ and by dissolution in hydrochloric acid.⁸ Antimony pentoxide reacts in a somewhat similar manner.⁹

From antimony trisulphide the trichloride may be obtained by the action of chlorine,¹⁰ hydrogen chloride (either in the gaseous form or in solution as described above), thionyl chloride,¹¹ sulphuryl chloride¹² and ammonium chloride.¹³ Concentrated hydrochloric acid reacts with antimony pentasulphide with formation of the trichloride.¹⁴ It is of interest to note that the trichloride has also been obtained by the distillation of a mixture of antimony sulphate and sodium chloride.¹⁵

Antimony pentachloride is reduced to the trichloride by heating with antimony.¹⁶

Stibine may be converted to antimony trichloride by the action of chlorine or phosphorus pentachloride.¹⁷

A pure solution of antimony trichloride may be prepared by dissolving antimony oxychloride in hydrochloric acid; crystals may be obtained by evaporation from a solution of the trichloride in carbon disulphide¹⁸ or in sulphuryl chloride, by sublimation of the trichloride in a current of carbon dioxide, and by solidification after fusion.

Antimony trichloride can exist in three distinct crystalline modifications¹⁹ with transition points at 65° C. and 69.5° C. respectively. The modification stable at the ordinary temperature crystallises in the rhombic system, forming colourless, transparent, prismatic or octahedral crystals.²⁰ Its density²¹ at 25° C. is 3.14. Its molecular volume²²

¹ Hensgen, *Chem. Zentr.*, 1891, 958.

² Heumann and Köchlin, *Ber.*, 1882, 15, 419, 1737; 1883, 16, 482, 1625; Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 425; Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 12.

³ L'Hôte, *Compt. rend.*, 1884, 98, 1491.

⁴ Attfield, *Zeitsch. anal. Chem.*, 1870, 9, 107; Dexter, *Pogg. Annalen*, 1857, 100, 568.

⁵ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 18; Robiquet, *Ann. Chim. Phys.*, 1817, [2], 4, 165.

⁶ Weber, *Pogg. Annalen*, 1861, 112, 625.

⁷ Oddo and Serra, *Gazzetta*, 1899, 29, II, 355; Michaelis, *loc. cit.*; Rauter, *Annalen*, 1892, 270, 251.

⁸ Robiquet, *loc. cit.*

⁹ Weber, *loc. cit.*; Rose, *Pogg. Annalen*, 1858, 105, 571; Michaelis, *J. prakt. Chem.*, 1871, 4, 454; Rauter, *loc. cit.*; Prinz, *Annalen*, 1884, 223, 358.

¹⁰ Rose, *Pogg. Annalen*, 1824, 3, 445.

¹¹ Prinz, *loc. cit.*

¹² Ruff, *Ber.*, 1901, 34, 1752.

¹³ Fresenius, *Zeitsch. anal. Chem.*, 1886, 25, 200; de Clermont, *Compt. rend.*, 1879, 88, 972.

¹⁴ Scherer, *Zeitsch. anal. Chem.*, 1864, [3], 206.

¹⁵ Berzelius, *Schweigger's J.*, 1812, 6, 144.

¹⁶ Hensgen, *loc. cit.*

¹⁷ Stock and Guttman, *Ber.*, 1904, 37, 885; Vogel, *J. prakt. Chem.*, 1838, 13, 57.

¹⁸ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 38, 72.

¹⁹ Kendall, Crittenden and Miller, *J. Amer. Chem. Soc.*, 1923, 45, 963.

²⁰ Topsoe, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, 66, 42; Cooke, *loc. cit.*; Groth, *Chem. Kryst.*, I, 227. For the spatial structure, see Bergmann and Engel, *Zeitsch. physikal. Chem.*, 1931, 13 B, 232.

²¹ *International Critical Tables*, 1926, 1, 111. See also Cohen and Strengers, *Zeitsch. physikal. Chem.*, 1905, 52, 164; Cooke, *loc. cit.*

²² Biltz, Sapper and Wünnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

(calculated from the density at -194° C. and the coefficient of expansion) is 68.5. It melts at 73.4° C., forming a colourless or yellowish oil.¹ The existence of the first transition point slightly below the melting point is indicated when the substance is heated gradually, for, in the neighbourhood of the melting point the crystals change to a heavy powder. The latent heat of fusion is 3,030 gram-calories per mole.² The density of the liquid, and the surface tension (σ), at various temperatures, are as follows :

Temperature, $^{\circ}$ C.	109.5	127.5	148.5	166.5
Density (D_4^t)	2.599	2.558	2.511	2.471
σ (dynes per cm.)	44.51	41.84	39.43	37.38

The variation of the density of the liquid with temperature (t)³ between 109° C. and 166° C. is thus given by the expression

$$D_4^t = 2.844 - 0.00224t$$

The calculated mean value for the parachor is 227.4.

Liquid antimony trichloride boils⁴ at 220.2° C., its latent heat of vaporisation⁵ being 10,700 calories per mole. The critical temperature is 524° C., the ratio of the boiling point to the critical temperature (on the absolute scale) thus being 0.619.⁶

Antimony trichloride may be distilled from solutions containing sulphuric acid provided that hydrobromic acid is dropped slowly into the solution, which latter should be kept at 180° C.⁷ On distilling a solution of antimony trichloride in hydrochloric acid, hydrogen chloride distils over first, followed by a mixture of hydrogen chloride and antimony chloride, and finally antimony chloride alone.⁸ The volatility of antimony trichloride is reduced by the addition of ferrous chloride.⁹ The trichloride does not volatilise when a current of hydrogen chloride is passed through a hot, dilute solution.¹⁰

The solubility of antimony trichloride in water and the effect of temperature upon solubility is as follows :¹¹

¹ Kendal, Crittenden and Miller, *loc. cit.* See also Cooke, *loc. cit.*; Kopp, *Annalen*, 1855, 95, 348; Capitaine, *J. prakt. Chem.*, 1839, 18, 449.

² Tolloczko, *Bull. Acad. Sci. Cracow*, 1901, 1; Tolloczko and Meyer, *Chem. Zentr.*, 1910, ii, 1024. For the specific heat, see Pebal and Jahn, *Pogg. Annalen*, 1886, [2], 27, 584.

³ Sugden, *J. Chem. Soc.*, 1927, 130, 1173. See also *International Critical Tables*, 1928, 3, 23; Kurnakov, Perlmutter and Kanov, *Annales de l'Institut Polytechnique Pierre-le-Grand, Petrograd*, 1915, 24, 399; Klemensiewicz, *Bull. Acad. Sci. Cracow*, 1908, 485.

⁴ Maier, *Bureau of Mines Tech. Paper*, 1925, 360. See also Capitaine, *loc. cit.*; Cooke, *loc. cit.*; Carnelley and Williams, *J. Chem. Soc.*, 1878, 33, 281; Anschütz and Evans, *J. Chem. Soc.*, 1886, 49, 708; *Ber.*, 1886, 19, 1994; *Annalen*, 1889, 253, 101.

⁵ Maier, *loc. cit.*

⁶ Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, 87, 635. See also van Aubel, *Bull. Acad. roy. Belg.*, 1922, 7, 469.

⁷ Rohre, *Zeitsch. anal. Chem.*, 1924, 65, 109; Böttger, *Oesterr. Chem. Zeit.*, 1924, 27, 24.

⁸ Rose, *Pogg. Annalen*, 1858, 105, 570; Schleier, *Inaug. Dissertation, Erlangen*, 1892.

⁹ Fischer, *Annalen*, 1881, 208, 189.

¹⁰ Hufschmidt, *Ber.*, 1884, 17, 2245; Gooch, Browning and Gruener, *Zeitsch. anal. Chem.*, 1893, 32, 473.

¹¹ van Bemmelen, Noodt and Meerburg, *Zeitsch. anorg. Chem.*, 1903, 33, 272. See also de Pauw, *Dissertation, Utrecht*, 1922.

Temperature, ° C. .	0	15	20	25	30	35	40	50	60	72
Solubility (Grams SbCl ₃ in 100 grams water)	601.1	815.8	920.8	988.1	1068	1152	1368	1917	4531	∞

When excess of water is employed, hydrolysis sets in rapidly, antimony trichloride thus resembling the other trichlorides of this group. The solubilities of the trichloride in aqueous solutions of hydrochloric acid at various concentrations at 20° C. are as follows (the concentration of each solute is given in grams per 100 grams of water) : ¹

HCl	0	4.86	12.84	16.80	18.41	28.68	58.08
SbCl ₃	910.1	895.4	879.0	857.6	866.4	856.3	789.8

The trichloride is soluble in many other solvents including ether,² carbon disulphide,³ absolute alcohol, acetone,⁴ chloroform,⁵ and to some extent in liquid cyanogen.⁶ It is insoluble in carbon tetrachloride.

The molal conductivity of solutions of antimony trichloride in bromine⁷ suggests that double molecules of Sb₂Cl₆ exist, which dissociate into Sb₂Cl₆⁺⁺⁺ and 3Cl⁻ ions. This view is supported by electrolysis experiments.⁸

The dielectric constant⁹ has been determined for a series of dilute solutions of antimony trichloride in benzene. At 25° C. the value varies with dilution from 2.377 to 2.588, and at 40° C. from 2.340 to 2.534. From this the calculated value of the dipole moment¹⁰ is 3.75×10^{-18} e.s.u.

The chlorides of potassium, rubidium, ammonium and thallium will dissolve in purified liquid antimony trichloride. When the concentration of the solution is above 0.1N, the conductivity is less than that of a corresponding aqueous solution; for more dilute solutions the conductivity is greater. The conductivity increases regularly with rise of temperature from 70° C. to 200° C. It is probable that the degree of ionisation is less for solutions in antimony trichloride than for solutions in water, but that for the dilute solutions the ionic velocity is greater.¹¹ Solutions of the bromides of potassium, ammonium and thallium in

¹ Seidel, "Solubilities of Inorganic and Organic Substances" (New York), 2nd Ed., 1920, p. 88; Meerburg, *Zeitsch. anorg. Chem.*, 1903, 33, 290.

² Usanovitch and Terpugov, *J. Gen. Chem. Russ.*, 1932, 2, 447; *Zeitsch. physikal. Chem.*, 1933, 165 A, 39.

³ Cooke, *loc. cit.*

⁴ Naumann, *Ber.*, 1904, 37, 4332.

⁵ Sabanejew, *Zeitsch. Chem.*, 1871, 7, 204.

⁶ Centnerswer, *Ber. russ. Phys. Ges.*, 1901, 33, 545; *Bull. Soc. chim.*, 1901, [3], 28, 405.

⁷ Plotnikov and Kudra, *Zeitsch. physikal. Chem.*, 1929, 145 A, 265.

⁸ For the conductivities of solutions of antimony trichloride in other solvents, see Kahlenburg and Lincoln, *J. Physical Chem.*, 1899, 3, 26; Lincoln, *ibid.*, 1901, 5, 503.

⁹ Smith, *Proc. Roy. Soc.*, 1932, 136 A, 256.

¹⁰ Slightly different values have also been obtained, according to the method of calculation adopted. See Malone and Ferguson, *J. Chem. Physics*, 1934, 2, 94; Bergmann and Engel, *Physikal. Zeitsch.*, 1931, 32, 507; *Zeitsch. physikal. Chem.*, 1931, 13 B, 232; Werner, *Zeitsch. anorg. Chem.*, 1929, 181, 154; Schlundt, *J. Physical Chem.*, 1901, 5, 157, 503; 1909, 13, 669.

¹¹ Klemensiewicz, *loc. cit.* See also Frycz and Tolloczko, *Chem. Zentr.*, 1913, i, 91.

antimony trichloride have also been examined and their conductivities determined.¹

The viscosity of antimony trichloride from 80° to 200° C. has been determined,² and the curve obtained by plotting the fluidity against the temperature appears to show a break at 120° C.

The Raman spectrum,³ which consists of four lines, suggests the existence of co-valent linkages.

The refractive index⁴ for the sodium *D* line is 1.460.

The vapour pressure of antimony trichloride⁵ is as follows :

<i>t</i> ° C.	120	130	140	150	160
<i>p</i> (mm.)	29	43	64	92	127

Determinations of the vapour density of antimony trichloride⁶ are in agreement with the molecular formula, SbCl₃; this formula is also confirmed by a number of determinations of the molecular weight in solution by the freezing point method.⁷

The heat of formation of antimony trichloride⁸ is 91,390 gram-calories per mole.

The trichloride can be distilled without decomposition in a current of hydrogen.⁹

The reaction between antimony trichloride and hydrogen has been investigated by passing a current of hydrogen at the rate of two litres per hour over the chloride.¹⁰ By means of a transformer a pressure of 15,000 volts was applied to the reaction chamber, and an antimony mirror was obtained.

The trichloride is stated to absorb oxygen when exposed to the air; certainly it deliquesces rapidly in air, forming a cloudy liquid, while a solution of antimony trichloride in hydrochloric acid readily absorbs

¹ Klemensiewicz and Balouna, *Roczniki Chem.*, 1931, 11, 683; 1930, 10, 481.

² Klemensiewicz, *Bull. Acad. Sci. Cracow*, 1908, 485.

³ Daure, *Compt. rend.*, 1928, 187, 940; Krishnamurti, *Nature*, 1930, 125, 892.

⁴ Becquerel, *Ann. Chim. Phys.*, 1877, [5], 59, 122.

⁵ *International Critical Tables*, 1928, 3, 213. See also Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, 87, 635.

⁶ Mitscherlich, *J. prakt. Chem.*, 1840, [1], 19, 455; Worcester, *Proc. Amer. Acad. Arts Sci.*, 1883, 18, 61.

⁷ Raoult, *Zeitsch. physikal. Chem.*, 1888, 2, 371; Lespiau, *Compt. rend.*, 1897, 125, 1094; Tolloczko, *Zeitsch. physikal. Chem.*, 1899, 30, 705. See, however, Walden (*Zeitsch. anorg. Chem.*, 1902, 29, 377; *Zeitsch. physikal. Chem.*, 1903, 43, 437), who obtained higher results by the freezing point method.

For further information concerning the physical properties of antimony trichloride, see Werner, *Zeitsch. anorg. Chem.*, 1929, 181, 154; Chipman and McIntosh, *Proceedings and Transactions of the Nova Scotia Institute of Science*, 1928, 16, 189; von Müllenheim, *Zeitsch. anorg. Chem.*, 1928, 176, 1; Quam and Wilkinson, *J. Amer. Chem. Soc.*, 1925, 47, 989; Schuster, *Zeitsch. anorg. Chem.*, 1925, 146, 299; Gossmann, *Zeitsch. Physik.*, 1924, 22, 273; Macbeth and Maxwell, *J. Chem. Soc.*, 1923, 123, 370; Biltz, *Zeitsch. physikal. Chem.*, 1922, 100, 152; Rideal, *Phil. Mag.*, 1921, [6], 42, 156; Crymbal, *Proc. Chem. Soc.*, 1914, 30, 179; Pascal, *Bull. Soc. chim.*, 1912, [4], 11, 201; Schlundt, *J. Physical Chem.*, 1901, 5, 503.

⁸ Thomsen, *Ber.*, 1883, 16, 39. See also Guntz, *Ann. Chim. Phys.*, 1884, [6], 3, 53; Tolloczko, *Zeitsch. physikal. Chem.*, 1899, 30, 705; Tolloczko and Meyer, *Kosmos*, 1910, 35, 641; Thomlinson, *Chem. News*, 1909, 99, 133.

⁹ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 60, 72.

¹⁰ Miyamoto, *J. Chem. Soc. Japan*, 1932, 53, 788.

oxygen.¹ Oxidation occurs under the influence of sunlight, and it is suggested that a peroxide is formed at an intermediate stage.²

As already stated, the trichloride will dissolve in a minimum quantity of water without decomposition, but if the molecular proportion of H_2O to $SbCl_3$ exceeds 2 to 1, oxychlorides are formed, the compositions of which depend upon the temperature and the concentration.³ (For the hydrolysis of antimony trichloride, see p. 66.)

Fluorine displaces chlorine from antimony trichloride, the action being vigorous.⁴

Thermal examination of the system $SbCl_3 - Cl_2$ indicates the presence of a compound,⁵ $SbCl_3 \cdot 2Cl_2$, which freezes at $-81.5^\circ C$. Antimony pentachloride is also formed. With nitrosyl chloride the compound⁶ $SbCl_3 \cdot NOCl$ has been obtained. No compound of antimony trichloride with bromine is indicated by thermal examination.

Antimony trichloride is decomposed when heated with sulphur, grey antimony trisulphide, Sb_2S_3 , being formed;⁷ a solution of the trichloride in hydrochloric acid is not affected, however, when heated with sulphur.⁸

Hydrogen sulphide reacts with the vapour of antimony trichloride to form antimony trisulphide;⁹ reddish-brown crystals of *antimony thiochloride*, $SbSCl$, are also formed by this reaction at a slightly lower temperature.¹⁰ Amorphous antimony trisulphide is precipitated when hydrogen sulphide is passed through a solution of antimony trichloride in hydrochloric acid to which tartaric acid has been added;¹¹ in the absence of tartaric acid a thiochloride is formed.¹² Precipitation may also be effected from an ammoniacal solution containing tartaric acid,¹³ but not from a solution in acetone.¹⁴ Antimony trichloride dissolves in liquid hydrogen sulphide, the solution possessing appreciable conductivity; the properties of this solution suggest that complex compounds of antimony trichloride and hydrogen sulphide are formed.¹⁵

Concentrated sulphuric acid has very little action in the cold, but on warming, antimony sulphate is formed with evolution of hydrogen chloride.¹⁶ When a mixture of sulphuric acid and a solution of antimony trichloride in hydrochloric acid is distilled, hydrochloric acid distils over first, followed by antimony trichloride; when finally sulphuric acid distils over, no antimony is found in the distillate, there being a residue of antimony sulphate. By repeated distillations, however, it is possible to obtain all the antimony as trichloride.¹⁷

¹ Cooke, *Chem. News*, 1880, 44, 221.

² Brühl and Schlögel, *Zeitsch. anorg. Chem.*, 1934, 217, 401.

³ Brandes, *Schweigger's J.*, 1827, 51, 437; Weber, *Pogg. Annalen*, 1865, 125, 87; Sabanejew, *Zeitsch. Chem.*, 1871, 7, 204; *Bull. Soc. chim.*, 1871, [2], 16, 79; Baudrimont, *Compt. rend.*, 1856, 42, 863; *J. prakt. Chem.*, 1856, 69, 252.

⁴ Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 257.

⁵ Biltz and Jeep, *Zeitsch. anorg. Chem.*, 1927, 162, 32.

⁶ Gall and Mengdahl, *Ber.*, 1927, 60 B, 86.

⁷ Vogel, *Schweigger's J.*, 1817, 21, 70.

⁸ Vortmann and Padberg, *Ber.*, 1889, 22, 2644.

⁹ Durocher, *Compt. rend.*, 1851, 32, 823; Arctowski, *Zeitsch. anorg. Chem.*, 1895, 8, 220.

¹⁰ Ouvrard, *Compt. rend.*, 1893, 116, 1517.

¹¹ Rose, *Pogg. Annalen*, 1853, 89, 123.

¹² Duflos, *Archiv Apothekervereins nord. Deutschland*, 1828, 31, 94; 1829, 36, 278; *Schweigger's J.*, 1830, 22, 190; *Zeitsch. anal. Chem.*, 1871, 10, 343.

¹³ Finkener, *J. Soc. Chem. Ind.*, 1889, 8, 733.

¹⁴ Naumann, *Ber.*, 1904, 37, 4332.

¹⁵ Chipman and McIntosh, *Proc. and Trans. Nova Scotian Inst. Science*, 1928, 16, 189.

¹⁶ Vogel, *loc. cit.*; Friedrich, *Monatsh.*, 1893, 14, 519.

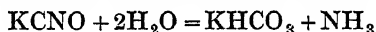
¹⁷ Rose, *Pogg. Annalen*, 1850, 105, 570.

When a solution of antimony trisulphide in boiling antimony trichloride is allowed to cool, a double compound, $\text{SbSCl}_3.7\text{SbCl}_3$, separates out in the form of yellow, transparent, rhombic prisms.¹ This substance is deliquescent, and is readily decomposed by heating or by the addition of water.

A number of compounds of antimony trichloride with alkyl sulphides and with alkyl sulphides and halides together have been prepared either by heating the components in a sealed tube at 90° to 120° C., or by heating them in calculated proportions gently under a reflux condenser.²

Ammonia reacts with molten antimony trichloride³ to form two *ammoniates*, namely $\text{SbCl}_3.\text{NH}_3$, from which all the ammonia can be removed by heating, and $\text{SbCl}_3.2\text{NH}_3$, a yellowish-white, crystalline substance which is stable and volatile. The former of these is much less deliquescent than the trichloride. From these compounds the corresponding double salts $\text{SbCl}_3.\text{NH}_4\text{Cl}$ and $\text{SbCl}_3.2\text{NH}_4\text{Cl}$ may be formed by the action of hydrochloric acid.⁴ A *tri-ammoniate*, $\text{SbCl}_3.3\text{NH}_3$, has been prepared by the action of ammonia on a solution of antimony trichloride in acetone.⁵ It is a white solid, stable in air; on heating it loses ammonia.⁶ More recently, however, it has been shown that when treated with liquid ammonia, one molecule of antimony trichloride absorbs rather more than three molecules of ammonia without appearing to form a definite ammoniate.⁷ With liquid ammonia, in fact, antimony trichloride yields a yellow compound⁸ to which the formula $\text{Sb}(\text{NH})\text{Cl}$ has been ascribed. On further treatment an orange *nitride*, SbN , is obtained (p. 113).

When potassium cyanate is added to an aqueous solution of antimony trichloride,⁹ a crystalline precipitate of antimonic acid is obtained. This is ascribed to the ammonia arising from the reaction



Nitric oxide, free from nitrogen peroxide, is without action upon a solution of antimony trichloride in chloroform, but in the presence of a trace of the peroxide, a complex crystalline precipitate is obtained. Solid antimony trichloride absorbs nitric oxide, the mixture becoming liquid. From this liquid all the nitric oxide can be removed by treatment in a vacuum.¹⁰

Antimony trichloride is oxidised by nitric acid, antimonic acid being formed.¹¹ When a solution of antimony trichloride in nitric acid is distilled, the first distillate consists of a mixture of hydrochloric acid and nitric acid; towards the end some antimony pentachloride distils with partial decomposition; antimony pentoxide remains.¹²

¹ Schneider, *Pogg. Annalen*, 1858, 108, 407.

² Rây, Adhikari and Ray, *J. Indian Chem. Soc.*, 1931, 8, 251, 711. See this Series, Vol. XI, Part III.

³ See also this Series, Vol. X.

⁴ Dehérain, *Compt. rend.*, 1861, 52, 734.

⁵ Naumann, *Ber.*, 1904, 37, 4332.

⁶ See also Jacquelin, *Ann. Chim. Phys.*, 1837, 66, 128; Poggiale, *Compt. rend.*, 1845, 20, 1180; *Annalen*, 1845, 56, 243; Weinland and Schmid, *Ber.*, 1905, 38, 1084; Rose, *Ann. Chim. Phys.*, 1836, [2], 62, 322.

⁷ Schwarz and Jeanmaire, *Ber.*, 1932, 65 B, 1662.

⁸ Schwarz and Jeanmaire, *loc. cit.*

⁹ Dalietos, *Praktika (Akad. Athenon)*, 1931, 6, 92; *Zeitsch. anorg. Chem.*, 1934, 217, 381.

¹⁰ Thomas, *Compt. rend.*, 1895, 120, 1115; 1896, 123, 51; Besson, *ibid.*, 1889, 108, 1012.

¹¹ Vogel, *Schweigger's J.*, 1817, 21, 70.

¹² Rose, *Ann. Chim. Phys.*, 1836, [2], 62, 322.

When phosphine is passed through molten antimony trichloride, a black complex substance of indefinite composition is obtained.¹

Phosphorus pentachloride² reacts with formation of the double compound $\text{PCl}_5 \cdot \text{SbCl}_5$. A reaction also occurs with phosphorus triiodide.³

When antimony trichloride is heated with alcohol under pressure, oxychlorides are formed;⁴ the reactions with ether,⁵ acetone,⁶ dimethylamine,⁷ benzene,⁸ aniline⁹ and many other organic compounds¹⁰ have also been described.¹¹

Antimony trichloride reacts with stannic iodide,¹² double decomposition taking place. Double decomposition occurs when antimony trichloride is heated with germanium tetraiodide.¹³

A violet compound of copper, Cu_2Sb , is obtained by the action of a hydrochloric acid solution of antimony trichloride containing cuprous chloride upon metallic copper. The reactants should be protected from the air.¹⁴ A similar reaction occurs between antimony trichloride and metallic tin,¹⁵ the compound Sb_2Sn being formed. No reaction has been observed with bismuth.

Reactions also occur with nickel¹⁶ and cobalt,¹⁷ a mono-antimonide being produced in each case.

Among the uses for which antimony trichloride has been suggested is that of an addition to a hydrocarbon fuel to act as an "antiknock." About 18 grains per gallon of petrol are recommended.¹⁸

Double and Complex Compounds.—When a current of hydrogen chloride is passed into a saturated aqueous solution of antimony trichloride at 0° C., until no more of the gas can be absorbed, a compound

¹ Mahn, *Jenaische Zeitsch.*, 1869, 5, 160.

² Weber, *Pogg. Annalen*, 1865, 125, 78.

³ Karantassis, *Ann. Chim.*, 1927, 8, 71.

⁴ Schäffer, *Annalen*, 1869, 152, 135; *Ber.*, 1868, 1, 135; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 63, 105.

⁵ Nicklés, *Compt. rend.*, 1861, 52, 396; Sabanejew, *Zeitsch. anal. Chem.*, 1871, 10, 205; Kurnakov, Perlmutter and Kanov, *J. Russ. Phys. Chem. Soc.*, 1916, 48, 1658.

⁶ Kurnakov, Perlmutter and Kanov, *loc. cit.*

⁷ Vincent, *Zeitsch. anal. Chem.*, 1880, 19, 479.

⁸ Rosenheim and Stellmann, *Ber.*, 1901, 34, 3383; Menschutkin, *Chem. Zentr.*, 1910, ii, 378; *J. Chim. Phys.*, 1911, 9, 314.

⁹ Higbee, *Amer. Chem. J.*, 1900, 23, 150; Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1128.

¹⁰ Smith, *Ber.*, 1879, 12, 1420; Godeffroy, *Zeitsch. anal. Chem.*, 1877, 16, 244; Smith and Davis, *J. Chem. Soc.*, 1882, 41, 411; Claesson, *Bull. Soc. chim.*, 1876, [2], 25, 185; Köhler, *Ber.*, 1881, 14, 1626; Causse, *Bull. Soc. chim.*, 1892, [3], 7, 242; Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1275, 1303, 1329, 1785, 1805; 1912, 44, 1079, 1102, 1108, 1113, 1137; 1913, 45, 1710; Dunning and Reid, *J. Amer. Chem. Soc.*, 1927, 49, 2869; von Euler and Hellsbrom, *Svensk Kem. Tids.*, 1929, 41, 11; von Euler and Willstaedt, *Archiv Kemi, Mineral., Geol.*, 1929, 10 B, No. 9, 1; Montignie, *Bull. Soc. chim.*, 1929, 45, 302; Raudnitz, *Ber.*, 1927, 60 B, 743; Gray, *J. Chem. Soc.*, 1926, 129, 3174; Vanstone, *ibid.*, 1914, 105, 1491; 1925, 127, 550; Vasilief, *J. Russ. Phys. Chem. Soc.*, 1917, 49, 428; Belladen and Astengo, *Atti R. Accad. Lincei*, 1923, [5], 32, 1, 491; Vanino and Muschnug, *Ber.*, 1917, 50, 21; May, *J. Chem. Soc.*, 1912, 101, 1037.

¹¹ See also this Series, Vol. X; Vol. XI, Part III.

¹² Karantassis, *Ann. Chim.*, 1927, 8, 71.

¹³ Karantassis, *Compt. rend.*, 1933, 196, 1894.

¹⁴ Mazzucchelli and Vercillo, *Atti R. Accad. Lincei*, 1925, [6], 1, 233; Arrivaut, *Compt. rend.*, 1930, 190, 1506.

¹⁵ Mazzucchelli and Vercillo, *loc. cit.*

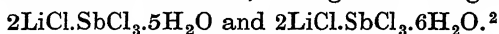
¹⁶ Vigouroux, *Compt. rend.*, 1908, 147, 976.

¹⁷ Ducelliez, *ibid.*, 1908, 147, 1048.

¹⁸ John, *U.S.A. Patent*, 1930, 1753294.

$2\text{SbCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ is obtained in the form of deliquescent crystals melting at 16°C . It loses hydrogen chloride on heating.¹

Many double salts with chlorides of the metals of Groups I, II and III have been described, among them being the following:

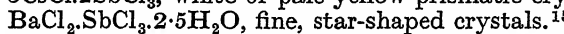
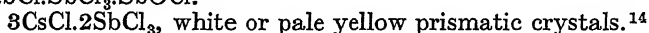


$\text{NaCl} \cdot \text{SbCl}_3$.³ It is possible that complexes, yielding ions of H_3SbCl_6 , are also formed when antimony trichloride is dissolved in solutions of sodium chloride.⁴

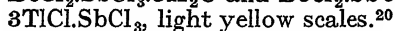
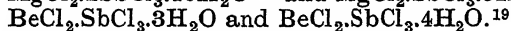
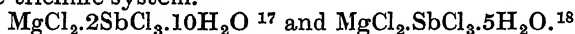
$2\text{KCl} \cdot \text{SbCl}_3$, dimorphic, crystallising in the hexagonal⁵ and the monoclinic systems.⁶ Crystals of the latter system have the following elements: $a : b : c = 0.7241 : 1 : 0.7222$; $\beta = 111^\circ 8'$. An hydrated form, $2\text{KCl} \cdot \text{SbCl}_3 \cdot 2\text{H}_2\text{O}$, has also been described.⁷ $2\text{KCl} \cdot \text{SbCl}_3 \cdot \text{SbOCl}$, prismatic crystals of the monoclinic system.⁸

$\text{KBr} \cdot \text{SbCl}_3 \cdot \text{H}_2\text{O}$, bright yellow octahedra; $3\text{KBr} \cdot 2\text{SbCl}_3 \cdot 2\text{H}_2\text{O}$, bright yellow rhombic crystals; $3\text{KBr} \cdot \text{SbCl}_3 \cdot 1.5\text{H}_2\text{O}$, yellow crystals of the tetragonal system:⁹ $a : c = 1 : 0.7629$.

$\text{RbCl} \cdot 2\text{SbCl}_3 \cdot \text{H}_2\text{O}$, long, colourless crystals (M.pt. 77°C .) of the monoclinic system:¹⁰ $a : b : c = 1.699 : 1 : 0.820$; $\beta = 90^\circ 31\frac{1}{2}'$. $\text{RbCl} \cdot \text{SbCl}_3$, colourless crystals (no definite M.pt.), monoclinic system:¹¹ $a : b : c = 1.732 : 1 : 1.085$; $\beta = 114^\circ 26'$. $3\text{RbCl} \cdot 2\text{SbCl}_3$, pale yellow crystals, trigonal rhombohedral system:¹² $a : c = 1 : 0.5625$; $\alpha = 110^\circ 54'$. $2\text{RbCl} \cdot \text{SbCl}_3 \cdot \text{SbOCl}$.¹³



$\text{CaCl}_2 \cdot \text{SbCl}_3 \cdot 8\text{H}_2\text{O}$, large, colourless, tabular crystals, probably of the triclinic system.¹⁶



$17\text{CdCl}_2 \cdot \text{SbCl}_3 \cdot 18\text{H}_2\text{O}$, relatively stable, colourless; $17\text{CoCl}_2 \cdot \text{SbCl}_3 \cdot 32\text{H}_2\text{O}$, violet; $\text{AlCl}_3 \cdot 3\text{SbCl}_3 \cdot 6\text{H}_2\text{O}$, very hygroscopic, unstable.²¹

¹ Engel, *Compt. rend.*, 1888, 106, 1797; Berthelot, *Ann. Chim. Phys.*, 1887, [6], 10, 133; Ditte, *ibid.*, 1881, [5], 22, 557.

² Ephraim, *Ber.*, 1903, 36, 1821.

³ Poggiale, *Compt. rend.*, 1845, 20, 1180; *Annalen*, 1845, 56, 244; Liebig, "Handwörterbuch der reinen und angewandten Chemie" (Braunschweig, 1837), Vol. I, p. 423.

⁴ Saylor, "Fifth Colloid Symposium Monograph," 1927, p. 49.

⁵ Benedict, *Proc. Amer. Acad. Arts Sci.*, 1894, 22, 212.

⁶ Benedict, *loc. cit.*; Poggiale, *Compt. rend.*, 1845, 20, 1180; *Annalen*, 1845, 56, 243.

⁷ See also Herty, *Amer. Chem. J.*, 1894, 16, 495; Wells and Foote, *Amer. J. Sci.*, 1897, [4], 3, 461; Jordis, *Ber.*, 1903, 36, 2539; Miyake, *Mem. Coll. Eng. Kyushu*, 1925, 3, 187.

⁸ Benedict, *loc. cit.*

⁹ Atkinson, *J. Chem. Soc.*, 1883, 43, 289; Herty, *loc. cit.*

¹⁰ Wheeler, *Amer. J. Sci.*, 1893, [3], 46, 269; *Zeitsch. anorg. Chem.*, 1893, 5, 253.

¹¹ Wheeler, *loc. cit.*; Remsen and Saunders, *Amer. Chem. J.*, 1892, 14, 155.

¹² Wheeler, *loc. cit.*; Remsen and Saunders, *loc. cit.* See also Godefroy, *Ber.*, 1875, 8, 11; Wells and Foote, *loc. cit.*

¹³ Wells and Foote, *loc. cit.*

¹⁴ Godefroy, *Ber.*, 1874, 7, 375; 1875, 8, 9; Remsen and Saunders, *loc. cit.*; Setterberg, *Ofvers K.-Vet.-Akad. Forh.*, 1862, 6, 26; Muthmann, *Ber.*, 1893, 26, 1425; Behrens, *Zeitsch. anal. Chem.*, 1891, 30, 163.

¹⁵ Poggiale, *loc. cit.*

¹⁶ Benedict, *Proc. Amer. Acad. Arts Sci.*, 1895, 30, 9; *Zeitsch. anorg. Chem.*, 1895, 8, 234.

¹⁷ Ephraim, *loc. cit.*; Poggiale, *loc. cit.*

¹⁸ Ephraim, *loc. cit.*

¹⁹ Ephraim, *loc. cit.*

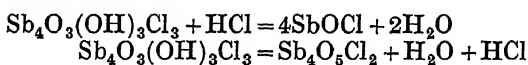
²⁰ Ephraim and Barteczko, *Zeitsch. anorg. Chem.*, 1909, 61, 238.

²¹ Saucieu, *Bull. Soc. Chim. Romania*, 1931, 13, 23.

Thermal examination of a number of binary systems, involving antimony trichloride as one of the components, has been made. Among them the following may be mentioned :

$\text{SbCl}_3\text{--LiCl}$, $\text{SbCl}_3\text{--NaCl}$, $\text{SbCl}_3\text{--KCl}$,¹ $\text{SbCl}_3\text{--KBr}$,² $\text{SbCl}_3\text{--NH}_4\text{Cl}$, $\text{SbCl}_3\text{--CuCl}$, $\text{SbCl}_3\text{--AgCl}$,³ $\text{SbCl}_3\text{--BaCl}_2$, $\text{SbCl}_3\text{--HgCl}_2$, $\text{SbCl}_3\text{--HgBr}_2$; $\text{SbCl}_3\text{--AlCl}_3$; $\text{SbCl}_3\text{--SnCl}_2$, $\text{SbCl}_3\text{--SnCl}_4$,⁴ $\text{SbCl}_3\text{--SnBr}_4$,⁵ $\text{SbCl}_3\text{--SnI}_4$,⁶ $\text{SbCl}_3\text{--AsCl}_3$, $\text{SbCl}_3\text{--AsBr}_3$,⁷ $\text{SbCl}_3\text{--SbCl}_5$,⁸ $\text{SbCl}_3\text{--SbBr}_3$, $\text{SbCl}_3\text{--SbI}_3$,⁹ $\text{SbCl}_3\text{--BiCl}_3$.¹⁰

Oxychlorides of Tervalent Antimony.—Many substances of a complex nature, obtained by different investigators, have been described as oxychlorides of trivalent antimony;¹¹ a study of the hydrolysis of antimony trichloride, however, suggests that only two of these, namely SbOCl and $\text{Sb}_4\text{O}_5\text{Cl}_2$, are true compounds, although unstable intermediate products may be formed. The hydrolysis does not appear to be progressive, as was thought by early workers. It is probable that by the addition of sufficient water antimony trichloride is completely hydrolysed to a hydrated form of antimony trioxide and hydrochloric acid, the former of which forms a bulky, white, amorphous precipitate. On standing, this precipitate tends to adsorb hydrochloric acid, the composition of the resulting product depending upon the concentration of the supernatant solution. This adsorption product tends to change on standing for a considerable time into a very finely crystalline substance, the needle-shaped crystals of which may have the composition $\text{Sb}_4\text{O}_3(\text{OH})_3\text{Cl}_3$; these in turn are transformed to the oxychloride SbOCl . From the table on p. 67 it will be seen that the solid phase in equilibrium with concentrated mixtures of antimony trichloride and water is the oxychloride SbOCl , while that in equilibrium with more dilute mixtures is the oxychloride $\text{Sb}_4\text{O}_5\text{Cl}_2$. The two oxychlorides can be readily distinguished from one another by their crystalline form. It is suggested that the intermediate substance $\text{Sb}_4\text{O}_3(\text{OH})_3\text{Cl}_3$ reacts in accordance with the equations



It is possible that another intermediate unstable crystalline product, $\text{Sb}_4\text{O}_3(\text{OH})_5\text{Cl}$, may also be formed. The transition from SbOCl to $\text{Sb}_4\text{O}_5\text{Cl}_2$ takes place when the concentration of chlorine in the solution is approximately 8.0N; and the transition from antimony trioxide to an oxychloride when the chlorine concentration is about 0.1N. Examination of the equilibrium of the system $\text{Sb}_2\text{O}_3\text{--HCl--H}_2\text{O}$ at

¹ Kendal, Crittenden and Miller, *J. Amer. Chem. Soc.*, 1923, 45, 963.

² Tolloczko, *Zeitsch. physikal. Chem.*, 1899, 30, 705.

³ Kendal, Crittenden and Miller, *loc. cit.*

⁴ Kendal, Crittenden and Miller, *loc. cit.*; Tolloczko, *Bulletin internationale de l'Académie des Sciences de Cracovie*, 1901, 1, 1.

⁵ Tolloczko, *loc. cit.*

⁶ Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 96.

⁷ Tolloczko, *loc. cit.*; Garelli and Bassani, *Atti R. Accad. Lincei*, 1901, 101, 255.

⁸ Aten, *Zeitsch. physikal. Chem.*, 1909, 68, 41; Moles, *ibid.*, 1915, 90, 70.

⁹ Bernardis, *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 438.

¹⁰ Tolloczko, *loc. cit.*

¹¹ Schneider, *Pogg. Annalen*, 1859, 108, 407; Sabanejew, *Zeitsch. Chem.*, 1871, [2], 7, 204; Williams, *Chem. News*, 1871, 24, 224; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 63, 105; Frenzel, *Jahresber.*, 1877, 31, 1286; Merz and Weith, *Ber.*, 1880, 13, 210.

25° C. revealed no transition points corresponding to the formation of oxychlorides.¹

**EQUILIBRIUM IN THE SYSTEM $\text{Sb}_2\text{O}_3\text{--HCl--H}_2\text{O}$
AT 25° C.**

Chlorine, gram-atoms per litre.	Antimony, gram-atoms per litre.	Chlorine, gram-atoms per litre.	Antimony, gram-atoms per litre.
0.198	0.00012	2.10	0.0522
0.402	0.000172	2.29	0.0755
0.601	0.000298	2.54	0.120
0.799	0.000610	2.81	0.177
1.02	0.00124	3.36	0.309
1.32	0.00565	3.85	0.440
1.56	0.0116	4.79	0.745
1.74	0.0194	5.93	1.13
1.90	0.0299		

EQUILIBRIUM IN THE SYSTEM $\text{SbCl}_3\text{--H}_2\text{O}$ AT 25° C.

Solid and Liquid Phases in Equilibrium at Different
Concentrations.

Liquid Phase.		Solid Phase.	
Antimony, per cent.	Chlorine, per cent.	Antimony, per cent.	Chlorine, per cent.
44.0	41.9	69.9	20.7
39.4	38.8	70.0	20.6
33.0	34.5	69.8	20.7
28.7	31.6	70.0	20.6
27.1	30.4	69.9	20.6
23.8	27.9	70.1	20.7
21.2	25.8	70.0	20.7
18.7	23.7	..	20.7
16.2	21.4	Mixture of Crystals	
14.8	20.7		
11.3	17.5	76.1	11.3
7.5	14.3	76.1	11.2
4.5	11.7	76.1	11.3
1.9	9.0	76.0	11.1
1.7	8.9	76.2	11.2

Note.— SbOCl contains Sb 70.29 per cent.; Cl 20.47 per cent.

$\text{Sb}_4\text{O}_5\text{Cl}_2$ contains Sb 76.34 per cent.; Cl 11.15 per cent.

¹ Lea and Wood, *J. Chem. Soc.*, 1924, 125, 137. See also van Bemmelen, Noodt and Meerburg, *Zeitsch. anorg. Chem.*, 1903, 33, 272, 289; Berthelot, *Ann. Chim. Phys.*, 1887, [6], 10, 133; Le Chatelier, *Compt. rend.*, 1885, 100, 737; 1886, 102, 1388; Ditte, *ibid.*, 1874, 79, 956.

As the conditions of equilibrium within the system $\text{SbCl}_3\text{--H}_2\text{O--HCl}$ (or of the more complete system $\text{Sb}_2\text{O}_3\text{--H}_2\text{O--HCl}$) do not appear to have been fully elucidated, it may be desirable to include here the results of investigations by previous workers. In the table below data are included for three different temperatures, namely 15°C ,¹ 20°C .² and 50°C .³ For each temperature the formulæ of the stable solid phases are stated, together with the composition, or range of composition, of the liquid phase in equilibrium therewith.⁴ It will be noted that the existence of an oxychloride $\text{Sb}_3\text{O}_2\text{Cl}_5$ or $\text{SbCl}_3\cdot(\text{SbOCl})_2$, indicated by these investigations, has not been confirmed by the more recent work of Lea and Wood referred to on p. 67.

EQUILIBRIUM IN THE SYSTEM $\text{SbCl}_3\text{--HCl--H}_2\text{O}$.

(The composition of the liquid phase in each case is recorded as moles of solute in 100 moles of water.)

Solid Phases.

Liquid Phase.

Temperature 15°C .

SbOCl	{HCl	3.66	4.40	4.78	4.85	5.20	5.24
	{ SbCl_3	0.08	0.27	0.89	2.56	4.75	6.68
$\text{Sb}_4\text{O}_5\text{Cl}_2$	{HCl	0.425	0.46	2.0	2.76		
	{ SbCl_3	0.0009	0.0015	0.0029	0.0167		

Temperature 20°C .

SbCl_3 ; $\text{Sb}_3\text{O}_2\text{Cl}_5$	{HCl	3.6					
	{ SbCl_3	68.3					
$\text{Sb}_3\text{O}_2\text{Cl}_5$; SbOCl	{HCl	9					
	{ SbCl_3	25					
SbCl_3	{HCl	2.4	6.1	8.3	8.2	9.1	11.7
	{ SbCl_3	71.2	69.9	68.2	68.7	68.9	68.1
$\text{Sb}_3\text{O}_2\text{Cl}_5$	{HCl	6.7	7.8	8.2			
	{ SbCl_3	64	50	35			
SbOCl	{HCl	7.3	8.4				
	{ SbCl_3	8.6	19.7				

Temperature 50°C .

SbOCl	{HCl	3.35	3.82	4.24		
	{ SbCl_3	0.172	0.896	2.640		
$\text{Sb}_4\text{O}_5\text{Cl}_2$	{HCl	0.18	1.58	2.00	2.76	
	{ SbCl_3	0.0008	0.008	0.012	0.046	

Hydrolytic dissociation is retarded and may be inhibited by the presence of hydrogen chloride, the chlorides of alkali and alkaline earth metals, and tartaric acid.⁵

¹ Le Chatelier, *loc. cit.*

² van Bemmelen, Noodt and Meerburg, *loc. cit.*

³ Le Chatelier, *loc. cit.*

⁴ Abegg, "*Handbuch der Anorganischen Chemie*" (Leipzig), 1917, Vol. III, Part 3, p. 596.

⁵ Watson, *J. Soc. Chem. Ind.*, 1886, 5, 590; Watson, *Chem. News*, 1888, 58, 297; Sanderson, *German Patent*, 1890, 54219; Causse, *Compt. rend.*, 1891, 113, 1042.

Antimony Oxychloride, or *Antimonyl Chloride*, SbOCl , is obtained as an amorphous white powder, or in the form of small rhombohedral crystals, by the hydrolysis of antimony trichloride at the ordinary temperature as already described, care being taken to avoid excess of water.¹ By heating antimony trichloride with alcohol in a sealed tube at 160°C ., antimony oxychloride is also obtained in the form of colourless crystals of the monoclinic system:² $a : b : c = 0.8934 : 1 : 0.7577$; $\beta = 108^\circ 29'$.

The heat of formation from the elements is 89,700 gram-calories per mole.³

When heated this oxychloride decomposes, yielding first $\text{Sb}_4\text{O}_5\text{Cl}_2$ and SbCl_3 , ultimately, with strong heating, passing into a mixture of antimony trioxide and antimony trichloride. Volatilisation of antimony trichloride begins at 170°C .⁴ Hot water converts antimonyl chloride into $\text{Sb}_4\text{O}_5\text{Cl}_2$.⁵

Antimonyl chloride is insoluble in alcohol and ether, but soluble in carbon disulphide, chloroform and benzene, as well as in hydrochloric acid and in a solution of tartaric acid.

The *oxychloride* $\text{Sb}_4\text{O}_5\text{Cl}_2$ may conveniently be prepared by methods similar to those adopted for SbOCl , using a moderate excess of water for hydrolysis, or by heating with alcohol at 140° to 150°C .⁶

This second oxychloride is obtained in the form of minute prismatic crystals of the monoclinic system:⁷ $a : b : c = 1.234 : 1 : 3.081$; $\beta = 121^\circ 2'$. Its density is 5.014. It melts without decomposition; but at a higher temperature it is decomposed into a mixture of the trichloride and the trioxide. It is not affected by cold water, but it loses chlorine when treated repeatedly with boiling water, while water at 150°C . decomposes it completely, antimony trioxide being formed.⁸ It is also converted into the oxide by treatment with alkali solutions. Mineral acids convert it into the corresponding normal salts, oxalic acid into a basic oxalate.⁹ When heated with sulphur it is converted into black antimony trisulphide, with evolution of sulphur dioxide; intermediate products may also be formed.¹⁰ The heat of formation from the elements is 328,800 gram-calories.¹¹

The following compounds of tervalent antimony, chlorine and sulphur, in addition to those previously mentioned (see p. 62), have been described.¹² Some of them may perhaps be thiochlorides: SbSbSbCl_3 , $\text{Sb}_4\text{S}_5\text{Cl}_2$, $\text{Sb}_5\text{S}_6\text{Cl}_3$ and $\text{Sb}_6\text{S}_{11}\text{Cl}_2$.

¹ Sabanejew, *loc. cit.*; Péligot, *Ann. Chim. Phys.*, 1847, [3], 20, 283; *Annalen*, 1847, 64, 281; Williams, *loc. cit.*; Cooke, *loc. cit.*; Frenzel, *loc. cit.*; Schäffer, *Annalen*, 1869, 152, 135; *Ber.*, 1868, 1, 135.

² Schäffer, *loc. cit.*; Cooke, *loc. cit.* ³ Guntz, *Ann. Chim. Phys.*, 1884, [6], 3, 56.

⁴ Schäffer, *loc. cit.*; Sabanejew, *loc. cit.*; Cooke, *loc. cit.*

⁵ Sabanejew, *loc. cit.*

⁶ Sabanejew, *loc. cit.*; Johnston, *New Edinburgh Philosophical Journal*, 1835, 18, 40; *J. prakt. Chem.*, 1835, 6, 55; Malaguti, *Ann. Chim. Phys.*, 1835, 59, 220; *J. prakt. Chem.*, 1835, 6, 253; Péligot, *loc. cit.*; MacIvor, *Chem. News*, 1875, 32, 229; Schäffer, *loc. cit.*; Cooke, *loc. cit.*

⁷ Sabanejew, *loc. cit.*; Cooke, *loc. cit.*

⁸ Henry, *J. Pharm.*, 1826, 12, 79; Duflos, *Schweigger's J.*, 1833, 67, 268; Malaguti, *loc. cit.*; Debray, *Compt. rend.*, 1864, 58, 1209; *J. prakt. Chem.*, 1866, 98, 151.

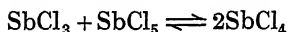
⁹ Behrens, *Zeitsch. anal. Chem.*, 1891, 30, 163; Schäffer, *loc. cit.*; Sabanejew, *loc. cit.*

¹⁰ Grouvelle, *Schweigger's J.*, 1821, 33, 431.

¹¹ Guntz, *loc. cit.*

¹² Ouvrard, *Compt. rend.*, 1893, 116, 1517; Ruff and Fischer, *Ber.*, 1904, 37, 4515; Taverne, *Chem. Weekblad*, 1908, 5, 19.

Antimony Tetrachloride, SbCl_4 .—This compound does not yet appear to have been isolated, but many double compounds formed from it have been obtained, including $2\text{CsCl}.\text{SbCl}_4$, $2\text{RbCl}.\text{SbCl}_4$, $\text{TiCl}.\text{SbCl}_4$ and possibly $3\text{KCl}.\text{SbCl}_4$. Many other compounds contain both trivalent and quadrivalent antimony; while still more are known only in the form of isomorphous mixtures with corresponding compounds such as platinum tetrachloride and tin tetrachloride. All these compounds are dark brown or deep violet in colour, a darkening of colour being an indication of the presence of quadrivalent antimony.¹ All these double compounds, with the exception of one containing both thallic and thalious chlorides,² with the probable formula $\text{TiCl}.\text{TiCl}_3.2\text{SbCl}_4$, tend to decompose into mixtures of compounds containing trivalent and quinquevalent antimony.³ The equilibrium, in solution,



appears to be greatly dependent upon the temperature and the possibility of ionisation.⁴ The presence of sulphuric acid and of salts favours the formation of antimony tetrachloride, and the mixture becomes darker, indicating an increasing proportion of the tetrachloride, upon addition of hydrochloric acid, or with stronger heating.

Antimony Pentachloride, SbCl_5 .—This compound was first obtained by Rose by the direct union of the elements, powdered antimony combining spontaneously with chlorine, with incandescence. No antimony trichloride is formed.⁵ It is usually prepared by saturating molten antimony trichloride with chlorine, and distilling under reduced pressure.⁶

Antimony pentachloride is a colourless or faintly yellow liquid, possessing a sharp odour; it fumes strongly in air. It melts⁷ at $3^\circ \text{C}.$, and yields, at lower temperatures, needle-shaped crystals.⁸ Between 15° and $68^\circ \text{C}.$ the density is stated to be given by⁹

$$D_4^t = 2.392 - 0.00204t$$

Under reduced pressure it can be boiled without decomposition, the boiling point at different pressures being indicated in the following table:¹⁰

Pressure (mm.).	14	22	68
B.pt. ($^\circ\text{C}.$)	68	79	102–108

¹ Weinland and Schmid, *Ber.*, 1905, 38, 1080; Wells and Metzger, *Amer. Chem. J.*, 1906, 26, 268. See also Bosc, *J. Chem. Soc.*, 1895, 67, 516.

² Ephraim and Barteczko, *Zeitsch. anorg. Chem.*, 1909, 61, 238.

³ Ephraim and Weinberg, *Ber.*, 1909, 42, 4447.

⁴ Ephraim and Weinberg, *loc. cit.*

⁵ Rose, *Pogg. Annalen*, 1824, 3, 443.

⁶ Anschütz and Evans, *Ber.*, 1886, 19, 1994. See also Rose, *Pogg. Annalen*, 1858, 105, 571; Langguth, *Chimie et Industrie*, 1931, 25, 22.

⁷ Moles, *Anal. Fis. Quim.*, 1914, 12, 314.

⁸ Kammerer, *Ber.*, 1875, 8, 507.

⁹ Sugden, *J. Chem. Soc.*, 1927, 130, 1173; Moles, *loc. cit.*; Haagen, *Pogg. Annalen*, 1867, 131, 122; Ruff and Plato, *Ber.*, 1904, 37, 679.

¹⁰ Anschütz and Evans, *Annalen*, 1889, 253, 95. See also Moles, *Zeitsch. physikal. Chem.*, 1915, 90, 70. For other physical properties, see Becquerel, *Ann. Chim. Phys.*, 1877, [5], 12, 34; Schlundt, *J. Physical Chem.*, 1901, 5, 503; Bleekrode, *Wied. Annalen*, 1878, 3, 179; Walden, *Zeitsch. anorg. Chem.*, 1900, 25, 219; *Zeitsch. physikal. Chem.*, 1903, 43, 435; Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 99; Anschütz and Evans, *Annalen*, 1887, 239, 288; Nasu, *Bull. Chem. Soc. Japan*, 1934, 9, 198.

The dipole moment,¹ calculated from values obtained for the dielectric constant, is 1.14×10^{-18} e.s.u. (In connection with this the molecular structure has been discussed.)

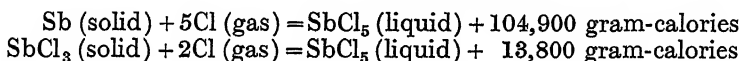
The Raman effect has been investigated,² both for antimony pentachloride and for chlorantimonic acid HSbCl_6 .

Investigation of the boiling points of solutions of antimony pentachloride in carbon tetrachloride and in chloroform indicates that some dissociation occurs in dilute solutions.³

The chemiluminescence produced when antimony powder is dropped into chlorine has been investigated.⁴ Two continuous bands were observed, at 6250–5200 Å. (max. 5950 Å.) and 4950–3930 Å. (max. 4650 Å.). No antimony lines could be detected.

The behaviour of antimony pentachloride as a solvent has been investigated.⁵ Chlorine, bromine, stannic chloride, chromyl chloride and chromic acid dissolve in normal fashion; iodine trichloride and gold trichloride undergo dissociation, and iodine, stannic bromide and stannic iodide react with the solvent.

The heat of formation of antimony pentachloride⁶ is as follows:



By exposure to moist air, or by the addition of the required amount of water, a crystalline *monohydrate*, $\text{SbCl}_5 \cdot \text{H}_2\text{O}$, is obtained;⁷ this hydrate may be purified by recrystallisation from chloroform. Its melting point lies between 87° and 92° C.; under reduced pressure it can be distilled with decomposition, the pentachloride being evolved at first, followed by a little trichloride; a non-volatile residue is left. When heated under atmospheric pressure chlorine is evolved.⁸ The hydrate is decomposed by water and by a solution of sodium carbonate. When heated with chloroform or carbon tetrachloride, phosgene is formed.

A *tetrahydrate*, $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$, has been obtained either by evaporating a saturated aqueous solution of the pentachloride over concentrated sulphuric acid,⁹ or by precipitation from a solution in chloroform.¹⁰

With excess of water hydrolysis of the pentachloride occurs, with formation of antimonic and hydrochloric acids; this hydrolysis can be prevented by the addition of concentrated hydrochloric acid, or of a solution of tartaric acid; in the former case, however, chlorantimonic acid is formed.

Antimony pentachloride dissociates on heating, forming the trichloride and chlorine,¹¹ the dissociation being slow at 120° C. but

¹ Bergmann and Engel, *Zeitsch. physikal. Chem.*, 1931, 13 B, 232.

² Redlich, *Naturwissenschaften*, 1932, 20, 365; Redlich, Kurz and Rosenfeld, *Zeitsch. physikal. Chem.*, 1932, 19 B, 231.

³ Moles, *Zeitsch. physikal. Chem.*, 1915, 90, 70.

⁴ Bhatnagar and Mathur, *Zeitsch. physikal. Chem.*, 1930, 9 B, 229.

⁵ Moles, *loc. cit.*

⁶ Thomsen, *Ber.*, 1883, 16, 40. See also Braune and Tiedje, *Zeitsch. anorg. Chem.*, 1926, 152, 39.

⁷ Anschütz and Evans, *Annalen*, 1887, 239, 287.

⁸ Daubrawa, *Annalen*, 1877, 186, 118.

⁹ Weber, *Pogg. Annalen*, 1865, 125, 86.

¹⁰ Anschütz and Evans, *loc. cit.* See also Kosmann, *Chem. Zeit.*, 1887, 11, 1058.

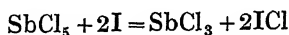
¹¹ Braune and Tiedje, *loc. cit.*

complete just above 300° C. Between 120° and 260° C. the dissociation constant is given by

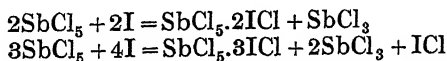
$$\log K = 9.74 - \frac{3570}{T}$$

The heat of the reaction is given as 16,320 gram-calories.

With iodine, three main reactions can take place, all of which are probably complex.¹ When less than 1.5 per cent. of iodine is dissolved in antimony pentachloride the reaction may provisionally be represented by



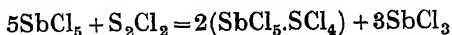
but iodine trichloride, antimony triiodide and a chloriodide of quinquivalent antimony may also be formed. There is, however, no evidence for the formation of the compound SbCl_5I . Two double compounds, $\text{SbCl}_5 \cdot 2\text{ICl}$ and $\text{SbCl}_5 \cdot 3\text{ICl}$, may also be obtained according to the equations



These reactions may be carried out by heating the equivalent proportions of antimony pentachloride and iodine at a temperature of 30° to 35° C. under a pressure of 15 mm. The existence of these double compounds has been confirmed by thermal examination.

When dry hydrogen sulphide acts upon antimony pentachloride a white crystalline compound, SbSbCl_3 , is formed.² It has a low melting point and is stable in dry air; it is decomposed by water into antimony oxychloride and sulphur, and by strongly heating into antimony trichloride and sulphur. It is attacked slowly by concentrated sulphuric acid with evolution of hydrogen chloride;³ it reacts also with chlorosulphonic acid.

Antimony pentachloride will react with sulphur monochloride,⁴ forming the compound $\text{SbCl}_5 \cdot \text{SbCl}_4$. A mixture of equal volumes of antimony pentachloride and sulphur monochloride is dissolved in sulphuryl chloride and the solution dried over phosphorus pentoxide. The equation is



The compound is obtained in the form of yellow-amber cubes with octahedral facets; it fumes strongly on exposure to air, becoming liquid with separation of sulphur. It melts at 157° to 163° C. It has no salt-like properties and is non-polar. A similar compound has been prepared by the action of sulphur tetrachloride⁵ on antimony pentachloride, and by chlorine on antimony trisulphide.⁶

The corresponding compounds with selenium tetrachloride,⁷ $\text{SbCl}_5 \cdot \text{SeCl}_4$, and with tellurium tetrachloride,⁸ $\text{SbCl}_5 \cdot \text{TeCl}_4$, have been obtained by the action of dry chlorine upon a fused mixture of antimony and selenium, or antimony and tellurium. The compound $\text{SbCl}_5 \cdot \text{SeOCl}_2$ has also been described.⁹

¹ Ruff, Zedner and Hecht, *Ber.*, 1915, 48, 2068.

² Cloëz, *Ann. Chim. Phys.*, 1850, [3], 30, 374.

³ Clausnizer, *Annalen*, 1879, 196, 295; Friedrich, *Monatsh.*, 1893, 14, 519.

⁴ Partington, *J. Chem. Soc.*, 1929, 132, 2573.

⁵ Ruff and Plato, *Ber.*, 1901, 34, 1749; 1904, 37, 4515.

⁶ Rose, *Pogg. Annalen*, 1837, 42, 532; Weber, *Pogg. Annalen*, 1865, 125, 78.

⁷ Weber, *Pogg. Annalen*, 1865, 125, 81, 328.

⁸ Moles, *loc. cit.*

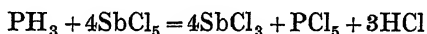
⁹ Weber, *loc. cit.*

Several addition compounds are formed with ammonia,¹ including a red triammoniate, $\text{SbCl}_5 \cdot 3\text{NH}_3$, a white, volatile tetrammoniate, $\text{SbCl}_5 \cdot 4\text{NH}_3$, and a hexammoniate, $\text{SbCl}_5 \cdot 6\text{NH}_3$. The first two of these ammoniates react with hydrochloric acid to form the corresponding ammonium chloride compound. The compound $\text{SbCl}_5 \cdot \text{NH}_4\text{Cl}$ may be obtained by heating together equivalent proportions of the binary compounds in a sealed tube.² The monohydrate, $\text{SbCl}_5 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$, has also been obtained.³ It crystallises in the rhombic system, and may be regarded as ammonium metachlorantimonate. Its crystal elements are : $a : b : c = 0.8909 : 1 : 0.7748$.

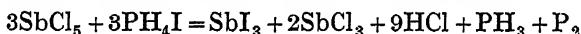
Antimony pentachloride reacts with nitric oxide and with nitrogen tetroxide forming the yellow, crystalline compounds $2\text{SbCl}_5 \cdot \text{NO}$ and $3\text{SbCl}_5 \cdot 2\text{NO}_2$ respectively. In each case the reactions are accompanied by considerable evolution of heat.⁴

With nitrosyl chloride, the compounds $\text{SbCl}_5 \cdot \text{NOCl}$ and $2\text{SbCl}_5 \cdot 5\text{NOCl}$ have been obtained.⁵

Phosphine⁶ reacts with antimony pentachloride, hydrogen chloride being evolved according to the equation



A mixture of the pentachloride and phosphonium iodide explodes violently in air, but when heated in a sealed tube a complex reaction takes place which may be represented by the equation⁷



Antimony pentachloride combines directly with phosphorus pentachloride,⁸ and with phosphorus oxychloride,⁹ forming the double compounds $\text{SbCl}_5 \cdot \text{PCl}_5$ and $\text{SbCl}_5 \cdot \text{POCl}_3$ respectively.

Reactions between antimony pentachloride and antimony pentafluoride have already been discussed (see p. 56).

With carbon disulphide a vigorous reaction takes place,¹⁰ which may be represented by the equation



If, however, the mixture is kept cold, the compound SbSbCl_7 is obtained.¹¹

Antimony pentachloride is reduced to the trichloride by the action of silicomethane.¹²

When antimony pentachloride is heated with germanium tetraiodide

¹ Rose, *Pogg. Annalen*, 1831, 24, 165; Persoz, *Ann. Chim. Phys.*, 1830, [2], 44, 322; Déherain, *Compt. rend.*, 1861, 52, 734. See also Rosenheim and Jacobsohn, *Zeitsch. anorg. Chem.*, 1906, 50, 307.

² Fireman, *J. Amer. Chem. Soc.*, 1904, 26, 741.

³ Weinland and Feige, *Ber.*, 1903, 36, 251; Weinland and Schlegelmilch, *Ber.*, 1901, 34, 2633.

⁴ Besson, *Compt. rend.*, 1889, 109, 1012.

⁵ Weber, *Pogg. Annalen*, 1864, 123, 347; Sudborough, *J. Chem. Soc.*, 1891, 59, 661; van Heteren, *Zeitsch. anorg. Chem.*, 1900, 22, 278.

⁶ Mahn, *Jenaische Zeitsch.*, 1869, 5, 159; Rose, *Pogg. Annalen*, 1831, 24, 165.

⁷ Fireman, *Amer. Chem. J.*, 1903, 30, 118.

⁸ Weber, *Pogg. Annalen*, 1865, 125, 78; Köhler, *Ber.*, 1880, 13, 875.

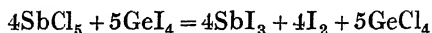
⁹ Weber, *loc. cit.*

¹⁰ Hofmann, *Annalen*, 1861, 115, 264.

¹¹ Bertrand and Finot, *Bull. Soc. chim.*, 1880, [2], 34, 201. See also Husemann, *Annalen*, 1861, 117, 229.

¹² Mahn, *Jenaische Zeitsch.*, 1869, 5, 248.

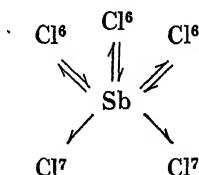
a reaction occurs which results in the formation of antimony triiodide and the liberation of iodine : ¹



Thermal investigation of the binary system TiCl_4 – SbCl_5 indicates the formation of a eutectic ² containing approximately 40 per cent. antimony pentachloride (M.pt. $-50^\circ \text{C}.$).

Gold chloride will dissolve in antimony pentachloride, but no compound appears to be formed.³

The parachor for antimony pentachloride is 26 units below the sum of the atomic constants ; ⁴ it is assumed, therefore, that there are two singlet linkages, and the formula,



is analogous to that ascribed to phosphorus pentachloride.⁵ In this formula each bond indicates a shared electron, while the superscript figures give the number of unshared electrons. In certain organic compounds antimony pentachloride is thought to exhibit an asymmetrical configuration.⁶

Chloroantimonic Acids.—Complex compounds are known to which the formulæ HSbCl_6 , H_2SbCl_7 , and H_3SbCl_8 have been ascribed ; these may be regarded as meta-, pyro- and ortho-chlorantimonic acids respectively,⁷ analogous to the corresponding oxyacids, HSbO_3 , $\text{H}_4\text{Sb}_2\text{O}_7$, and H_3SbO_4 , respectively. Neither the ortho- nor the pyro-chlorantimonic acid appears to have been isolated, although salts are known. *Meta-chlorantimonic acid* has been obtained by dissolving antimony trioxide in concentrated hydrochloric acid and saturating the solution with chlorine. The solution darkens at first, afterwards changing to a bright greenish-yellow colour. Crystals can be obtained by concentrating slightly over a water-bath, adding hydrochloric acid and leaving over sulphuric acid, the temperature not being allowed to exceed $0^\circ \text{C}.$ The crystals are very hygroscopic ; they are soluble in cold water, alcohol, acetone and glacial acetic acid. The solution in water undergoes hydrolysis, especially on warming, hydrated antimony pentoxide separating out. Hydrolysis is prevented, however, by hydrochloric acid, and to some extent by nitric acid. The solutions in organic solvents are more stable. As a precipitate is not formed immediately on adding silver nitrate to a nitric acid solution, it is suggested that the

¹ Karantassis, *Compt. rend.*, 1933, 196, 1894.

² Nasu, *Bull. Chem. Soc. Japan*, 1933, 8, 195.

³ Lindet, *Compt. rend.* 1885, 101, 1494.

⁴ Sugden, *J. Chem. Soc.*, 1927, 130, 1173.

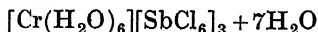
⁵ Prideaux, *Chem. and Ind.*, 1923, 42, 672.

⁶ Fischer and Taurinsch, *Zeitsch. anorg. Chem.*, 1932, 205, 309.

For the action of antimony pentachloride as a catalyst, see Whitby and Katz, *J. Amer. Chem. Soc.*, 1928, 50, 1160; Bothamley, *Trans. Faraday Soc.*, 1928, 24, 47; Knoll and Co. and Schmidt, *British Patent*, 1925, 250897.

⁷ Weinland and Feige, *Ber.*, 1903, 36, 244; Weinland and Schmid, *Zeitsch. anorg. Chem.*, 1905, 44, 37.

chlorine and antimony combine to form a complex ion.¹ On the grounds of the behaviour of the chromium salts of ortho- and meta-chlorantimonic acids towards hydrogen sulphide and towards silver nitrate, and also on account of the resemblance of these salts to the corresponding hydrated chlorides of chromium, the formulæ suggested for the complex chlorides of chromium and antimony are ²



and



Salts of all these chlorantimonic acids are prepared in a similar manner; in general, a mixture of the metallic chloride and antimony trichloride (or pentachloride) in dilute hydrochloric acid is saturated with chlorine; crystallisation is effected over sulphuric acid. All the salts are hydrolysed by cold water, with the exception of those of the alkali and alkaline earth metals, and even these yield antimony pentoxide on warming. The presence of hydrochloric acid renders the solutions more stable.

Salts which have been obtained are given in the following table, together with their crystallographic characteristics.³

(A) Salts of ortho-chlorantimonic acid.

$\text{CrSbCl}_6 \cdot 10\text{H}_2\text{O}$	Grey, hygroscopic plates.
$\text{FeSbCl}_6 \cdot 8\text{H}_2\text{O}$	Yellow, hygroscopic, four-sided tablets, tetragonal system ($a : c = 1 : 1.0112$).

(B) Salts of pyro-chlorantimonic acid.

$\text{MgSbCl}_7 \cdot 9\text{H}_2\text{O}$	Greenish-yellow, hygroscopic tablets; triclinic system ($a : b : c = 0.7144 : 1 : 2.595$; $\alpha = 100^\circ 22'$, $\beta = 88^\circ 3'$, $\gamma = 91^\circ 16'$).
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(C) Salts of meta-chlorantimonic acid.

$\text{LiSbCl}_6 \cdot 4\text{H}_2\text{O}$	Square, hygroscopic tablets.
$\text{KSbCl}_6 \cdot \text{H}_2\text{O}$	Greenish-yellow, six-sided, hexagonal plates; rhombic system ($a : b : c = 0.8889 : 1 : 0.7794$).
RbSbCl_6	Thin, six-sided, yellowish-green tablets, rhombic system ($a : b : c = 0.6719 : 1 : 0.8136$).
$\text{NH}_4\text{SbCl}_6 \cdot \text{H}_2\text{O}$	Isomorphous with the potassium salt ($a : b : c = 0.8909 : 1 : 0.8136$).
$\text{Be}(\text{SbCl}_6)_2 \cdot 10\text{H}_2\text{O}$	Small, yellowish, hygroscopic needles.
$\text{Ca}(\text{SbCl}_6)_2 \cdot 9\text{H}_2\text{O}$	Long, hygroscopic needles.
$\text{Zn}(\text{SbCl}_6)_2 \cdot 5\text{H}_2\text{O}$	Unstable.
$\text{Al}(\text{SbCl}_6)_3 \cdot 15\text{H}_2\text{O}$	Greenish-yellow, hygroscopic needles.
$\text{Cr}(\text{SbCl}_6)_3 \cdot 13\text{H}_2\text{O}$	Grey-violet, flat, hygroscopic needles.

The following complex compounds have also been prepared, their properties determined and their formulæ discussed:⁴ $\text{NaSbCl}_6 \cdot 3\text{H}_2\text{O} \cdot \text{NaCl}$; $\text{Cu}(\text{SbCl}_6)_2 \cdot 3\text{H}_2\text{O} \cdot \text{HSbCl}_6 \cdot 5\text{H}_2\text{O}$; $\text{Cd}(\text{SbCl}_6)_2 \cdot 12\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{SbCl}_5 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$; $\text{SbCl}_5 \cdot \text{C}_9\text{H}_7\text{N} \cdot \text{HCl}$.

¹ Weinland and Schmid, *loc. cit.*

² Pfeiffer, *Zeitsch. anorg. Chem.*, 1903, 36, 349.

³ Weinland and Feige, *loc. cit.*; Sauciu, *Bull. Soc. Chim. Romania*, 1931, 13, 23.

⁴ Sauciu, *Bull. Soc. Chim. Romania*, 1930, 12, 36.

The following compounds with ammonia¹ have also been obtained, in addition to a number of compounds with organic bases: $\text{Cu}(\text{SbCl}_6)_2 \cdot 5\text{NH}_3$; $\text{AgSbCl}_6 \cdot 2\text{NH}_3$; $\text{Zn}(\text{SbCl}_6)_2 \cdot 4\text{NH}_3$; $\text{Cd}(\text{SbCl}_6)_2 \cdot 7\text{NH}_3$; $\text{HSbCl}_6 \cdot 2\text{NH}_3$.

Antimonyl Perchlorate.—When a hot solution of antimony trioxide in excess of perchloric acid is allowed to cool, crystals of basic antimony perchlorate, or antimonyl perchlorate, $\text{SbO} \cdot \text{ClO}_4 \cdot 2\text{H}_2\text{O}$, separate out as small needles.²

Antimony and Bromine.

Antimony Tribromide, SbBr_3 , is formed spontaneously, and with incandescence, by the direct union of powdered antimony and bromine. For its preparation, bromine is placed in a retort, and excess of powdered antimony is added gradually, the mixture being kept cool until all the antimony has been added, after which the resulting antimony tribromide is distilled. It has also been prepared by the action of excess of antimony upon a solution of bromine in carbon disulphide. It may be purified by crystallisation from solution in the same solvent.³

Antimony tribromide forms colourless, acicular rhombic crystals

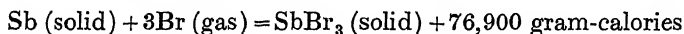
$$a : b : c = 0.817 : 1 : 0.869$$

Its density is 4.148; it melts at 96.6°C . and boils between 270° and 280°C .⁴

The molecular volume,⁵ calculated from the density at -194°C ., is 79.9.

The dipole moment (in solutions with organic solvents)⁶ is 2.47×10^{-18} e.s.u.

Antimony tribromide absorbs moisture from the air, and is immediately decomposed by it with the formation of an oxybromide. The formation of this oxybromide is prevented by addition of tartaric acid. The tribromide is not attacked by either nitric acid or sulphuric acid in the cold, but on warming bromine is liberated in each case.⁷ It is partially soluble in ether, forming two liquid layers, the lower of which contains a compound of the two substances. It is soluble in boron tribromide.⁸ Nitric oxide is without action, but with nitrogen tetroxide a compound, $2\text{Sb}_2\text{O}_5 \cdot \text{N}_2\text{O}_5$, is formed.⁹ The heat of formation¹⁰ is given by



¹ Weinland and Schmid, *loc. cit.*

² Fichter and Jenny, *Helv. Chim. Acta*, 1923, 6, 225.

³ Serullas, *Ann. Chim. Phys.*, 1828, 38, 322; *Pogg. Annalen*, 1828, 14, 112; Nicklés, *J. Pharm. Chem.*, 1862, [3], 41, 145; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 52; *Ber.*, 1880, 13, 951.

⁴ *International Critical Tables*, 1926, 1, 111. See also Kopp, *Annalen*, 1855, 95, 352; MacIvor, *Chem. News*, 1874, 29, 179; Anschütz and Weyer, *Annalen*, 1891, 261, 297. For other physical properties, see Pebal and Jahn, *Wied. Annalen*, 1886, 27, 584; Worcester, *Proc. Amer. Acad. Arts Sci.*, 1883, [2], 10, 61; Tolloczko, *Bull. Akad. Krakau*, 1901, 1; Garelli and Bassani, *Atti R. Accad. Lincei*, 1901, [5], 10, I, 255; Schlundt, *J. Phys. Chem.*, 1904, 8, 122; Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, 87, 635; Tolloczko and Meyer, *Chem. Zentr.*, 1910, ii, 1024; Isbekov and Plotnikov, *Zeitsch. anorg. Chem.*, 1911, 71, 328; Kurnakov, Krotkov and Oksman, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 558; 49, 585.

⁵ Biltz, Sapper and Wunnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

⁶ Malone and Ferguson, *J. Chem. Physics*, 1934, 2, 94.

⁷ Löwig, *Repertorium für die Pharmacie*, 1828, 29, 266.

⁸ Tarnbe, *Compt. rend.*, 1901, 132, 204.

⁹ Thomas, *Compt. rend.*, 1895, 120, 1116.

¹⁰ Guntz, *Compt. rend.*, 1885, 101, 161.

Complex Compounds of Antimony Tribromide.—A complex acid, $\text{H}_2\text{Sb}_3\text{Br}_{11}$, has been prepared by the action of hydrochloric acid on the salt $\text{K}_2\text{Sb}_3\text{Br}_{11}$ (see below). It is also obtained by the action of hydrobromic acid on a solution of antimony tribromide in acetone. It forms yellow crystals. Corresponding to this acid numerous salts of the alkali metals, the alkaline earth metals and cadmium have been prepared from solutions of the mixed bromides in acetone.¹ To these has been ascribed the general formula $\text{M}_2\text{Sb}_3\text{Br}_{11}$, where $\text{M} = \text{K}, \text{Na}, \text{Li}, \text{NH}_4(2\text{H}_2\text{O})$, and $\text{M}_2 = \text{Ba}(2\text{H}_2\text{O}), \text{Cd}$. Many of these salts are decomposed by water. From an examination of the electrolysis of their solutions² evidence has been obtained of the existence of the complex anion $\text{Sb}_3\text{Br}_{11}^-$ which subsequently dissociates into 3SbBr_3 and Br_2 . The compounds $\text{K}_2\text{Sb}_3\text{Br}_9\text{F}_2$, $\text{K}_2\text{Sb}_3\text{Br}_9\text{I}_2$, $\text{SrSb}_3\text{Br}_9\text{Cl}_2$, and $\text{HgSb}_6\text{Br}_{18}\text{I}_2$ have also been obtained.

By substituting potassium nitrate, potassium thiocyanate or sodium azide for the alkali halide, the compounds $\text{K}_2\text{Sb}_3\text{Br}_9(\text{NO}_3)_2$, $\text{K}_2\text{Sb}_3\text{Br}_9(\text{CNS})_2$ and $\text{NaSb}_3\text{Br}_9\text{N}_3$ have been obtained. The last is a white, crystalline substance.

In a similar manner the ammonium compound, $(\text{NH}_4)_2\text{SbBr}_5 \cdot 2\text{H}_2\text{O}$, is obtained in the form of hexagonal prisms.

A vanadium compound, $\text{SbBr}_3 \cdot \text{VBr}_4 \cdot 7\text{H}_2\text{O}$, has been obtained in the form of black, pointed prisms. It is hygroscopic and is decomposed by water.

A complex gold compound, $5\text{RbBr} \cdot \text{SbBr}_3 \cdot 2\text{AuBr}_3$, has been prepared. It is a black substance, soluble in water and in hydrobromic acid. It contains no univalent gold.³

Complex alkyl compounds have been obtained by treatment of antimony tribromide with mixtures of alkyl halides and alkyl sulphides.⁴ They appear to have the constitution $[\text{R}_3\text{S}]\text{SbBr}_4$.⁵

Antimony Oxybromides.—Two oxybromides have been described: *antimonyl bromide*, SbOBr , obtained by the action of light and air upon a solution of antimony tribromide in carbon disulphide,⁶ and $\text{Sb}_4\text{O}_5\text{Br}_2$, obtained either by hydrolysis of antimony tribromide,⁷ or by heating together antimony tribromide and absolute alcohol in a sealed tube.⁸ Antimonyl bromide is a brownish powder (the colour possibly being due to impurities) which on heating separates into two other substances. Continued heating converts it entirely into antimony trioxide. The compound $\text{Sb}_4\text{O}_5\text{Br}_2$ may be obtained in the form of monoclinic crystals, or as a white powder, which decomposes on heating, yielding antimony tribromide and antimony trioxide.

While *antimony tetrabromide* does not appear to have been isolated, a complex compound of this substance with ammonium bromide has been obtained by adding successively bromine and ammonium bromide to a solution of antimony tribromide in hydro-

¹ Vournasos, *Praktika, Akad. Athenon*, 1930, 5, 324; 1932, 7, 227; *Chem. Zentr.*, 1932, i, 1642.

² Vournasos, *Zeitsch. anorg. Chem.*, 1930, 192, 369.

³ Burkser, Rublov and Sharnovski, *ibid.*, 1929, 185, 144.

⁴ P. C. Rây, Adhikari and A. N. Rây, *J. Indian Chem. Soc.*, 1931, 8, 251.

⁵ For other complex bromides of organic bases, see Petzold, *Zeitsch. anorg. Chem.*, 1933, 215, 92.

⁶ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 104.

⁷ Cooke, *loc. cit.*; MacIvor, *Chem. News*, 1874, 29, 179; Serullas, *Ann. Chim. Phys.*, 1828, [2], 38, 322.

⁸ Cooke, *loc. cit.*

bromic acid.¹ It forms black octahedra of composition corresponding to $(\text{NH}_4)_2\text{SbBr}_6$. The rubidium salt, Rb_2SbBr_6 , has also been obtained, in the form of black, pointed, hygroscopic prisms. It is decomposed by water.²

Antimony Pentabromide, SbBr_5 , has not yet been isolated; its existence, however, is indicated by the action of antimony trihydride upon an aqueous solution of a mixture of bromine and potassium bromide,³ while molecular weight determinations on solutions in bromine by the boiling point method⁴ also suggest the existence of this compound. Complex compounds with organic bases have been prepared,⁵ in addition to many complex inorganic salts; these may perhaps be regarded as salts of bromoantimonic acids.

Of the three possible acids only one has been obtained in the free state. By crystallisation from a solution containing antimony tribromide, bromine and either hydrobromic or sulphuric acid the compound *meta-bromoantimonic acid*, $\text{HSbBr}_6 \cdot 3\text{H}_2\text{O}$, has been prepared in the form of hygroscopic, irregular, six-sided, black tablets. It decomposes readily, with evolution of bromine, leaving a residue of antimony tribromide.⁶ The following salts, corresponding to this acid, have also been prepared:

$\text{LiSbBr}_6 \cdot 4\text{H}_2\text{O}$	Black, square, hygroscopic tablets.
$\text{KSbBr}_6 \cdot \text{H}_2\text{O}$	Stout, six-sided, black tablets.
$\text{NH}_4\text{SbBr}_6 \cdot \text{H}_2\text{O}$	Resembles the potassium salt.
$\text{Fe}(\text{SbBr}_6)_3 \cdot 14\text{H}_2\text{O}$	Black, irregular, six-sided tablets; very hygroscopic.
$\text{Ni}(\text{SbBr}_6)_2 \cdot 12\text{H}_2\text{O}$	Black, glistening, irregular, six-sided tablets.

Other complex salts that have been described include:

$2\text{SbBr}_5 \cdot 3\text{CsBr} \cdot 2\text{H}_2\text{O}$	Black, microcrystalline powder.
$3\text{SbBr}_5 \cdot 2\text{BeBr}_2 \cdot 18\text{H}_2\text{O}$	Black, glistening prisms.
$5\text{SbBr}_5 \cdot 2\text{AlBr}_3 \cdot 24\text{H}_2\text{O}$	Black, glistening, stout prisms.

Some of the organic compounds suggest relationship with pyro-bromoantimonic acid.

Antimony and Iodine.

Antimony Triiodide, SbI_3 , is the only compound of antimony and iodine that is known to exist with certainty; a pentaiodide has been reported⁷ but subsequent investigations have failed to confirm its existence.⁸

Antimony triiodide may be obtained by synthesis; the combination of antimony with iodine is effected by triturating the two elements

¹ Ephraim and Weinberg, *Ber.*, 1909, 42, 4447.

² Weinland and Feige, *Ber.*, 1903, 36, 244.

³ Berthelot and Petit, *Compt. rend.*, 1889, 108, 546; *Ann. Chim. Phys.*, 1889, [6], 18, 67.

⁴ Beckmann, *Zeitsch. physikal. Chem.*, 1903, 46, 853.

⁵ Rosenheim and Stellmann, *Ber.*, 1901, 34, 3377.

⁶ Weinland and Feige, *Ber.*, 1903, 36, 244.

⁷ van der Espt, *Arch. Pharm.*, 1861, [2], 117, 115.

⁸ MacIvor, *Chem. News*, 1902, 86, 223; *J. Chem. Soc.*, 1876, 29, 328; Pendleton, *Chem. News*, 1883, 48, 97; Doornbosch, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 625; Jaeger and Doornbosch, *Zeitsch. anorg. Chem.*, 1912, 75, 261; Quercigh, *Atti R. Accad. Inst. Veneto Sci.*, 1912, 70, ii, 667.

together in a mortar; the heat generated by the reaction is usually sufficient to volatilise the triiodide produced, and the reaction may even become violently explosive if large quantities of materials are employed. The synthesis is more conveniently carried out by adding an excess of finely divided antimony gradually to iodine maintained at a gentle heat.¹ Combination of the two elements has also been effected by triturating with alcohol,² and by adding finely divided antimony to a solution of iodine in carbon disulphide. In the latter method the mixture is warmed until the colour of the iodine disappears and the triiodide is obtained by crystallisation from the solution.³

The compound has also been obtained by heating together equivalent proportions of antimony trisulphide and iodine, some thioiodide also being formed,⁴ and by adding potassium iodide either to a solution of antimony trichloride in acetone,⁵ or to an aqueous solution in the presence of dilute sulphuric acid.⁶

Four modifications of antimony triiodide have been described. Three of these are crystalline and one amorphous. The crystalline forms belong to the trigonal, rhombic and monoclinic systems respectively. The trigonal form appears to be the most stable at ordinary temperatures, but the conditions of equilibrium of the system are not fully understood. Transition points occur at 114° and 125° C., the former indicating an enantiomorphic change from trigonal form to the rhombic form, and the latter the transition from monoclinic to trigonal.⁷ Cohen, however, states that antimony triiodide is monotropic and the transition point at 114° C. is purely fortuitous.⁸ According to this view the rhombic form, which is obtained by sublimation, is a metastable phase which may exist unchanged for long periods even at low temperatures.

Trigonal antimony triiodide is obtained as reddish, hexagonal crystals whose colour varies with the method of preparation:

$$a = 7.466 \text{ \AA.}, \quad c = 20.892 \text{ \AA.}$$

There are six molecules in the unit cell.⁹ Its density is 4.848; it melts at 167° C., and boils¹⁰ between 414° and 427° C. It will dissolve in cold, concentrated hydrochloric acid; the solution on hydrolysis yields an oxyiodide. If, however, the solution in hydrochloric acid is boiled for a few seconds, the triiodide is converted into the trichloride and the solution on hydrolysis then yields an oxychloride. The triiodide is readily soluble in hydriodic acid, and from this solution a yellow oxyiodide is precipitated by hydrolysis. It is also soluble in boiling benzene,

¹ MacIvor, *J. Chem. Soc.*, 1876, 29, 328; *Chem. News*, 1874, 29, 255; Brandes, *Arch. Pharm.*, 1838, [2], 14, 135; 1839, [2], 17, 283; 1840, [2], 21, 319; Serullas, *J. Pharm. Chim.*, 1828, 14, 19; Berthelot, *ibid.*, 1828, 14, 615.

² Perrier and Lebrument, *Bull. Chim. appliquée*, 1862, 4, 254.

³ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 55, 77; Nicklés, *J. Pharm. Chim.*, 1862, [3], 41, 147.

⁴ Schneider, *Pogg. Annalen*, 1860, 109, 610.

⁵ Naumann, *Ber.*, 1904, 37, 4333. Also Fisk, *Amer. Mineral.*, 1930, 15, 263.

⁶ François, *Compt. rend.*, 1933, 196, 1398.

⁷ *International Critical Tables*, 1926, 1, 111; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1878, 5, 1, 72.

⁸ Cohen and Bruins, *Zeitsch. physikal. Chem.*, 1920, 94, 465.

⁹ Brækken, *Kgl. Norske Videnskab. Selskabs. Forh.*, 1929, 1930, No. 34, 123; *Zeitsch. Krist.*, 1930, 74, 67.

¹⁰ Carnelley and Williams, *J. Chem. Soc.*, 1878, 33, 281; Cooke and Bennett, *Chem. News*, 1881, 44, 255.

in carbon disulphide, in methylene iodide, in an aqueous solution of tartaric acid, and in arsenic tribromide; the solution in the last solvent is, however, unstable. With hexachlorethane it forms a dark brown solution which on cooling deposits first a lemon-yellow mass which ultimately changes to a red, crystalline substance. The triiodide is almost insoluble in chloroform, carbon tetrachloride and turpentine.¹

The dielectric constant² of solid antimony triiodide at 20° C. is 9.1; that of the liquid at 175° C. is 18.9. The dipole moment (in organic solvents)³ is 1.58×10^{-18} e.s.u.

The variation of the vapour pressure of liquid antimony triiodide with temperature is as follows: ⁴

Temperature, ° C.	250	265	280	295	310	325
Vapour pressure (mm.) . . .	23	35	53	80	115	166

Trigonal antimony triiodide is stable in air at ordinary temperatures. It sublimes quite readily; if the sublimation is carried out in the presence of air some decomposition occurs, iodine being liberated and some oxyiodide formed. It can be sublimed without decomposition in an atmosphere of hydrogen or carbon dioxide. It burns when heated in an atmosphere of oxygen, antimony trioxide being formed. In common with the other halides of antimony it is readily hydrolysed by water, yielding an insoluble, yellow oxyiodide;⁵ the reddish liquid which is also formed is stated to be a solution of antimony triiodide in hydriodic acid.

The triiodide reacts readily with chlorine with the formation of antimony trichloride and iodine monochloride; with bromine, antimony tribromide and iodine monobromide are similarly formed. By treatment with molten iodine monochloride the triiodide is converted into antimony trichloride and free iodine.

Cold, dilute sulphuric acid has very little action upon antimony triiodide, but if the acid is gently warmed a reaction takes place which results in the liberation of iodine and the formation of antimony sulphate. With hydrogen sulphide a reaction occurs at 150° C. and antimony triiodide is formed.

Antimony triiodide is readily attacked by concentrated nitric acid and is converted to antimony trioxide; free iodine and oxides of nitrogen are evolved. Dilute acid acts similarly, but more slowly. By reaction with ammonium hydroxide the triiodide is converted into a yellowish-white powder. Nitric oxide appears to have no action upon a mixture of the triiodide and chloroform,⁶ but nitrogen tetroxide attacks a mixture of the triiodide and ether with the formation of the compound $2Sb_2O_3 \cdot N_2O_5$. The triiodide is completely converted into trioxide by the action of alkali hydroxides and carbonates.

¹ MacIvor, *J. Chem. Soc.*, 1876, 29, 328; Retgers, *Zeitsch. anorg. Chem.*, 1893, 3, 344; *Zeitsch. physikal. Chem.*, 1893, 11, 340.

² *International Critical Tables*, 1929, 6, 76.

³ Malone and Ferguson, *J. Chem. Physics*, 1934, 2, 94.

⁴ Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, 87, 635. For other physical properties, see Worcester, *Proc. Amer. Acad. Arts Sci.*, 1883, [2], 10, 61; Biltz, Sapper and Wünnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

⁵ François, *Compt. rend.*, 1933, 196, 1398.

⁶ Thomas, *Compt. rend.*, 1895, 120, 117.

Antimony triiodide is partially soluble in both alcohol and ether, but the chief effect of both reagents is to convert it into an oxyiodide.

The molecular weight of antimony triiodide, determined by the elevation of the boiling point of various solvents, is abnormally low.¹ The solvents employed were the trichlorides of phosphorus, arsenic and antimony, and tin tetrachloride. Cryoscopic measurements using solutions in methylene iodide also yielded a low result.² This may be due to the formation of chemical compounds between the solvents and the solute, or to ionisation of the latter. It is interesting to note that a solution of antimony triiodide in arsenic triiodide has an appreciable conductivity, suggesting that ionisation has taken place.³

The heat of formation of trigonal antimony triiodide⁴ is 44,205 gram-calories.

When trigonal antimony triiodide is sublimed at a temperature of 114° C. or above, it is converted into the rhombic variety, which is obtained as small, greenish-yellow lamellæ, isomorphous with the corresponding trichloride and tribromide.

When a solution of the trigonal modification in carbon disulphide is exposed to bright sunlight for several hours, monoclinic antimony triiodide is obtained. Some oxyiodide and free iodine are formed at the same time. The monoclinic modification forms greenish-yellow, prismatic crystals:

$$a : b : c = 1.6408 : 1 : 0.6682 ; \quad \beta = 109^{\circ} 44'.$$

Its density (D_4^{22}) is 4.768. When heated to 125° C. it reverts to the trigonal modification.

Amorphous antimony triiodide⁵ is obtained by cooling a hot concentrated solution of the trigonal modification in glycerol. It may also be prepared by warming the trigonal modification with a small quantity of potassium acetate and excess of acetic acid; or by heating a mixture of antimony trioxide and potassium iodide with excess of acetic acid at 100° C. It is a yellow powder which melts at 172° C.

Double compounds of antimony triiodide and ammonium iodide have been prepared.⁶ The compounds $3\text{NH}_4\text{I} \cdot 4\text{SbI}_3 \cdot 9\text{H}_2\text{O}$ (bright red, rectangular prisms), $3\text{NH}_4\text{I} \cdot 2\text{SbI}_3 \cdot 3\text{H}_2\text{O}$ (thin rectangular or tetragonal leaves or plates of a dark reddish-brown or red colour),⁷ $4\text{NH}_4\text{I} \cdot \text{SbI}_3 \cdot 3\text{H}_2\text{O}$ (large, black, rectangular prisms), are formed by crystallisation from a mixed aqueous solution of the two iodides; in addition, the compound $\text{NH}_4\text{I} \cdot \text{SbI}_3 \cdot 2\text{H}_2\text{O}$ (red, tetragonal prisms) is obtained by the action of iodine on a saturated solution of ammonium chloride in contact with metallic antimony.⁸

Antimony triiodide also forms double salts with iodides of the alkali metals, the alkaline earth metals, and aluminium. They are usually prepared by dissolving the triiodide in a solution of the second iodide and crystallising out from the mixture,⁹ or by the action of antimony

¹ Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 96.

² Garelli and Bassani, *Gazzetta*, 1901, [1], 31, 407.

³ Walden, *Zeitsch. anorg. Chem.*, 1902, 29, 371.

⁴ *International Critical Tables*, 1929, 5, 180.

⁵ Vournazos, *Compt. rend.*, 1918, 166, 526.

⁶ Schäffer, *Pogg. Annalen*, 1860, 109, 613.

⁷ Caven, *Proc. Chem. Soc.*, 1905, 21, 187.

⁸ Nicklès, *Compt. rend.*, 1860, 51, 1097.

⁹ Schäffer, *Pogg. Annalen*, 1860, 109, 610; Welkow, *Ber.*, 1874, 7, 804.

upon a solution of iodine in alcohol in the presence of the second iodide.¹ For example, the compound $\text{SbI}_3 \cdot 2\text{KI} \cdot \text{H}_2\text{O}$ has been obtained by the former method.² They are obtained as reddish-black, transparent crystals, which are decomposed by heat, by water and by concentrated sulphuric acid; they will dissolve in hydrochloric and acetic acids.

Salts of a complex *antimony iodohydrobromic acid*, HSbBrI_3 , have been obtained³ by triturating equimolecular proportions of antimony triiodide and metallic bromide with a non-aqueous substance such as acetic acid or xylene. In this way orange-yellow crystals of sodium antimoniodobromide, NaSbBrI_3 , and potassium antimoniodobromide, KSbBrI_3 , have been obtained. The corresponding salts of ammonium and lithium, $\text{NH}_4\text{SbBrI}_3$ and LiSbBrI_3 , are darker in colour, while the zinc salt, $\text{Zn}(\text{SbBrI}_3)_2$, is obtained as brown, tabular crystals which are only slowly decomposed by water. The free acid has not been isolated.

Complex compounds of the type $\text{R}_3\text{S} \cdot \text{SbI}_4$ (where R represents an alkyl radical) have been obtained by the interaction of alkyl iodides, alkyl sulphides and antimony iodide. They are rather unstable; they dissolve in acetone, giving coloured solutions. Conductivity experiments suggest the presence in their solutions of complex ions, which, however, readily undergo dissociation.⁴

The following binary systems have been examined by thermal analysis: antimony triiodide-phosphorus triiodide,⁵ antimony triiodide-arsenic triiodide,⁶ antimony triiodide-arsenic tribromide,⁷ antimony triiodide-antimony trichloride,⁸ antimony triiodide-antimony pentachloride.⁹

Antimony Oxyiodide, or *Antimonyl Iodide*, SbOI , is obtained when a solution of antimony triiodide in carbon disulphide is exposed to bright sunlight in the presence of air. No action takes place in the dark unless ozone is present. It is an amorphous yellow powder, which decomposes at 150°C ., at which temperature antimony triiodide sublimes; sublimation ceases at 200°C ., the residue, another oxyiodide, $\text{Sb}_4\text{O}_5\text{I}_2$, remaining stable up to 350°C .¹⁰ The oxyiodide $\text{Sb}_4\text{O}_5\text{I}_2$ is also obtained when a solution of antimony triiodide in hydriodic acid is poured into boiling water.¹¹ It is a yellow powder which dissolves slowly in tartaric acid. It is decomposed when heated to a red heat, antimony triiodide being removed by sublimation, leaving a residue of antimony trioxide.¹² If a solution of potassium iodide is added to a very dilute solution of antimony trichloride in water containing a little sulphuric acid, a bright red precipitate of antimony triiodide is obtained. If insufficient sulphuric acid is present, however, an orange precipitate of $2\text{Sb}_2\text{O}_3 \cdot \text{SbI}_3$ is obtained by hydrolysis.¹³

¹ Nicklès, *loc. cit.*

² François, *Compt. rend.*, 1935, 200, 393.

³ Vournazos, *Compt. rend.*, 1922, 174, 164.

⁴ P. C. Rây, Adhikari and A. N. Ray, *J. Indian Chem. Soc.*, 1931, 8, 251.

⁵ Jaeger and Doornbosch, *Zeitsch. anorg. Chem.*, 1912, 75, 261.

⁶ Jaeger and Doornbosch, *loc. cit.*; Queroigh, *Atti R. Accad. Lincei*, 1912, 21 I, 415; Vasilief, *J. Russ. Phys. Chem. Soc.*, 1910, 44, 1076.

⁷ Walden, *loc. cit.*

⁸ Bernardis, *Atti R. Accad. Lincei*, 1912, [5], 21 II, 438.

⁹ Beckmann, *Zeitsch. anorg. Chem.*, 1907, 55, 175; Moles, *Zeitsch. physikal. Chem.*, 1915, 90, 70.

¹⁰ Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 63, 105.

¹¹ MacIvor, *Chem. News*, 1874, 29, 179.

¹² See also Serullas, *Ann. Chim. Phys.*, 1828, [2], 38, 322; Böttger and Brandes, *Arch. Pharm.*, 1839, [2], 17, 283.

¹³ François, *loc. cit.*

The product obtained by the action of water upon antimony triiodide is of variable composition depending upon the temperature and concentration.¹ There is some indication that a complex acid, $H_2(SbOI_3)$, is formed, the mercuric and cupric salts of this acid having been obtained. Mercuric antimony oxyiodide, $HgSbOI_3$, is prepared by warming a mixture of equimolecular proportions of mercuric cyanide and antimony triiodide in moist amyl alcohol upon a water-bath for four or six hours. It melts at $78^\circ C.$ and is decomposed by concentrated acids and by alkalis. It can, however, be recrystallised from solution in cold, dilute, hydrochloric acid. Cupric antimony oxyiodide, $CuSbOI_3$, is obtained by a similar reaction between cupric acetate and antimony triiodide.²

Another complex acid, $[Sb(IO_3)_3(OH)_3]H$, is stated to have been obtained by the action of antimony pentachloride upon an excess of iodic acid.³

Antimony Thioiodide, $SbSI$, is obtained by the action of antimony trisulphide on antimony triiodide,⁴ by the action of iodine upon antimony trisulphide,⁵ or by the action of hydrogen sulphide upon antimony triiodide heated to $150^\circ C.$ ⁶ It crystallises in small, dark red, lustrous, needle-shaped crystals of a form similar to those of kermesite. It melts at $392^\circ C.$ and above this temperature decomposes forming a mixture of trisulphide and triiodide. It is not decomposed by hot or cold water, or by dilute acids. Hydrogen sulphide is set free by the action of concentrated hydrochloric acid; sulphur and iodine by the action of concentrated nitric acid. Alkali hydroxides and carbonates remove iodine, leaving a residue of thioantimonites.

Several antimony iodocyanides have been obtained.⁷ By heating mercuric cyanide and antimony triiodide in dry xylene, mercuric antimony iodocyanide, $Hg[SbI_3(CN)_2]$, is obtained. Further heating results in the formation of trimercuric antimony iodocyanide, $Hg_3[Sb_2I_6(CN)_6]$; while the corresponding cuprous compound, $Cu_6[Sb_2I_6(CN)_6]$, is obtained in a similar manner.

Mixed Halides.—Several compounds which may be described as mixed halides have already been mentioned. Others have been prepared by various methods. The halides of the elements phosphorus, arsenic, antimony, titanium, tin and perhaps germanium, when mixed together, readily undergo reactions which involve an interchange of halogen atoms. The mixed halides so formed, however, have not been isolated.⁸

Antimony Trifluorodichloride, SbF_3Cl_2 , may be prepared by the action of chlorine upon antimony trifluoride⁹ at a temperature above $70^\circ C.$ The antimony trifluoride should be dissolved in antimony trichloride, pentachloride or tribromide. If treated with bromine or

¹ Serullas, *loc. cit.*; Berthemot, *J. Pharm. Chim.*, 1828, [2], 14, 615; Böttger and Brandes, *loc. cit.*

² Vournazos, *Compt. rend.*, 1920, 170, 1256.

³ P. Rây and S. N. Rây, *J. Indian Chem. Soc.*, 1926, 3, 110.

⁴ Schneider, *Pogg. Annalen*, 1860, 110, 150.

⁵ Ouvrard, *Compt. rend.*, 1893, 117, 108; Schneider, *Pogg. Annalen*, 1860, 109, 610.

⁶ François, *Compt. rend.*, 1934, 198, 1994; Ouvrard, *loc. cit.*

⁷ Vournazos, *loc. cit.*

⁸ Raeder, *Kgl. Norske Videnskab. Selskabs. Skrifter*, 1929, No. 3, 1.

⁹ Henne, *British Patent*, 1933, 389619; *United States Patent*, 1934, 1984480.

iodine, the corresponding compounds ¹ *antimony trifluorodibromide*, SbF_3Br_2 , and *antimony trifluorodiiodide*, SbF_3I_2 , are formed.

Antimony Bromodiiodide, SbBrI_2 , is formed by adding a solution of bromine in chloroform to a solution of ethyldiiodostibine in chloroform. It is obtained as long yellow crystals ² melting at 88°C .

By the interaction of mercuric bromide with antimony triiodide (preferably in the presence of a suitable organic solvent),³ the complex compound antimony mercuribromiodide, $\text{SbI}_3 \cdot 6\text{HgBr}_2$, has been obtained.

ANTIMONY AND OXYGEN.

Three oxides of antimony are known with certainty, namely antimony trioxide, Sb_2O_3 , antimony tetroxide, Sb_2O_4 , and antimony pentoxide, Sb_2O_5 ; a complex oxide, Sb_6O_{13} , may also exist.⁴ It is probable that some of the confusion which existed among earlier workers in connection with certain of the oxides of antimony may have been due to the extreme slowness with which equilibrium is obtained between antimony pentoxide and its decomposition products.⁵ Three of the oxides resemble one another very closely in crystal structure, one modification of each of them possessing a cubic lattice of the diamond type. The oxide Sb_6O_{13} may have a tetragonal lattice.⁶

Lower oxides of antimony have been described by early writers, but the evidence for the existence of these does not appear to have been confirmed.⁷

Antimony Trioxide, Sb_2O_3 .—This substance was known in ancient times; it is probably referred to by Pliny under the name of *stibia femina*, and by Basil Valentine under the name *flores Antimonii*. The latter name was subsequently applied to the product derived from the roasting of antimony sulphide. Antimony trioxide occurs naturally in the minerals senarmonite and valentinite, and in certain other more complex minerals (see p. 9).

The trioxide may be prepared by the direct oxidation of antimony, by heating in air or in water vapour; ⁸ by the action of concentrated nitric acid, in which case a mixture of oxides is obtained; ⁹ or by fusion with potassium nitrate and potassium bisulphate.¹⁰ The higher oxides of antimony may be reduced to the trioxide by the action of sulphur dioxide ¹¹ or hydriodic acid.¹²

When antimony trisulphide is roasted, a mixture of oxides of antimony is obtained, from which the trioxide can be separated by

¹ Frigidaire Co., *French Patent*, 1932, 732320.

² Clark, *J. Chem. Soc.*, 1930, 133, 2737.

³ Vournazos, *J. prakt. Chem.*, 1933, 136, 41.

⁴ Simon and Thaler, *Zeitsch. anorg. Chem.*, 1927, 162, 253.

⁵ Simon and Thaler, *loc. cit.*

⁶ Dehlinger and Glocker, *Zeitsch. anorg. Chem.*, 1927, 165, 41; Simon, *Zeitsch. anorg. Chem.*, 1927, 165, 31; Dehlinger, *Zeitsch. Krist.*, 1927, 66, 108; Bozorth, *J. Amer. Chem. Soc.*, 1923, 45, 1621; Dehlinger, *Zeitsch. physikal. Chem.*, 1929, B. 6, 127.

⁷ Berzelius, *Schweigger's J.*, 1812, 6, 144; 1818, 22, 69; Jones, *J. Chem. Soc.*, 1876, 29, 642; Marchand, *J. prakt. Chem.*, 1845, 34, 381; Bottger, *ibid.*, 1856, 68, 372; Proust, *Gilbert's Annalen*, 1807, 25, 186.

⁸ Baker and Dixon, *Proc. Roy. Soc.*, 1888, 45, 1; Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 362; Debray, *Compt. rend.*, 1864, 58, 1209.

⁹ Brandes, *Arch. Pharm.*, 1840, [2], 21, 156; Preuss, *Annalen*, 1839, 31, 197; Rose, *Pogg. Annalen*, 1841, 53, 161; Berzelius, *Schweigger's J.*, 1812, 6, 144; 1818, 22, 69.

¹⁰ Preuss, *loc. cit.*

¹¹ von Knorre, *Zeitsch. angew. Chem.*, 1888, 1, 155.

¹² Bunsen, *Annalen*, 1858, 106, 1.

fusion with more antimony trisulphide.¹ The trioxide may also be obtained from the trisulphide by treatment with concentrated sulphuric acid, followed by the addition of an alkali carbonate to the solution obtained.²

Many antimony compounds may be decomposed by suitable reagents, yielding antimony trioxide. Thus, antimonyl chloride is completely converted to the trioxide by treatment with water at 150° C.;³ antimony salts are decomposed by alkali hydroxides and carbonates, and potassium antimonyl tartrate is decomposed by the action of salts of weak acids such as borates, acetates, thiosulphates, phosphates, sulphites, etc.,⁴ trioxide being formed in each case.

Technical antimony trioxide, as used in the manufacture of paints, is frequently obtained direct from antimony ores or concentrates.⁵

Antimony trioxide is dimorphous, the two modifications crystallising in the cubic and rhombic systems respectively. Both modifications occur naturally, the cubic as senarmontite and the rhombic as valentinite; both can also be produced artificially, the cubic by sublimation and the rhombic by the hydrolysis of solutions of antimony trichloride.⁶ Although both modifications can exist unchanged for long periods at the ordinary temperature, the cubic modification is the stable form, the rhombic form being stable at higher temperatures. In support of this view, it is found that a specimen of antimony trioxide after prolonged heating at 550° C. yields cubic crystals only; after similar treatment at 590° C. rhombic crystals only are obtained. Rhombic crystals separate from the melt on crystallisation, but these are completely converted to cubic crystals by prolonged heating at 550° C. At a temperature of about 570° C. both cubic and rhombic crystals are in equilibrium under the pressure of their own vapour. The transition temperature is therefore at approximately 570° C., the cubic modification being stable below this temperature and the rhombic above.⁷ Further support for this view is afforded by an examination of the vapour pressure curves of the two modifications (fig. 2);⁸ the computed transition point, however, appears to be slightly lower than the value recorded above.

Cubic antimony trioxide (senarmontite) contains eight molecules of Sb_4O_6 in the unit cell⁹

$$a = 11.14 \text{ \AA.}$$

Its density determined by pyknometer¹⁰ is 5.19, by X-rays, 5.49. Its hardness on Mohs' scale is 2.0 to 2.5. The specific heat¹¹ is 0.093 gram-

¹ Berzelius, *loc. cit.*; Shakhov and Slobodska, *Tsvet. Met.*, 1930, 1294; *Chimie et Industrie*, 1931, 25, 1126.

² Hornung, *J. Pharm. Chim.*, 1848, [3], 13, 355; Lindner, *Zeitsch. Chem.*, 1869, 5, 442; *Bull. Soc. chim.*, 1869, [1], 12, 455; Durand, *J. Pharm. Chim.*, 1842, [3], 2, 364.

³ Debray, *Compt. rend.*, 1864, 58, 1209; *J. prakt. Chem.*, 1866, 98, 151.

⁴ Long, *J. Amer. Chem. Soc.*, 1895, 17, 87.

⁵ Listrat, *U.S. Patent*, 1932, 1873774; Antimon Berg- und Hüttenwerke A.-G., *French Patent*, 1930, 706371; Deutsche Schmelz- und Raffinierwerke A.-G. and H. W. Grimm, *British Patent*, 1930, 348138; *French Patent*, 1930, 696448.

⁶ Terrell, *Ann. Chim. Phys.*, 1866, [4], 7, 350; Pasteur, *ibid.*, 1848, [3], 24, 442; 1850, [3], 28, 56; 1851, [3], 31, 67; Mitscherlich, *J. prakt. Chem.*, 1840, 19, 455; Rose, *Pogg. Annalen*, 1832, 26, 180; von Bonsdorff and Mitscherlich, *ibid.*, 1828, 15, 453.

⁷ Roberts and Fenwick, *J. Amer. Chem. Soc.*, 1928, 50, 2134.

⁸ Hincke, *ibid.*, 1930, 52, 3869.

⁹ Dehlinger, *Zeitsch. Krist.*, 1927, 66, 108.

¹⁰ Simon, *Zeitsch. anorg. Chem.*, 1927, 165, 31.

¹¹ *International Critical Tables*, 1929, 5, 95. See also Neumann, *Ann. Physik*, 1865, 126, 123; Regnault, *Ann. Chim. Phys.*, 1841, 1, 129.

calories per gram. The melting point is approximately 650°C. , and the calculated molar latent heat of fusion (assuming the molecule to

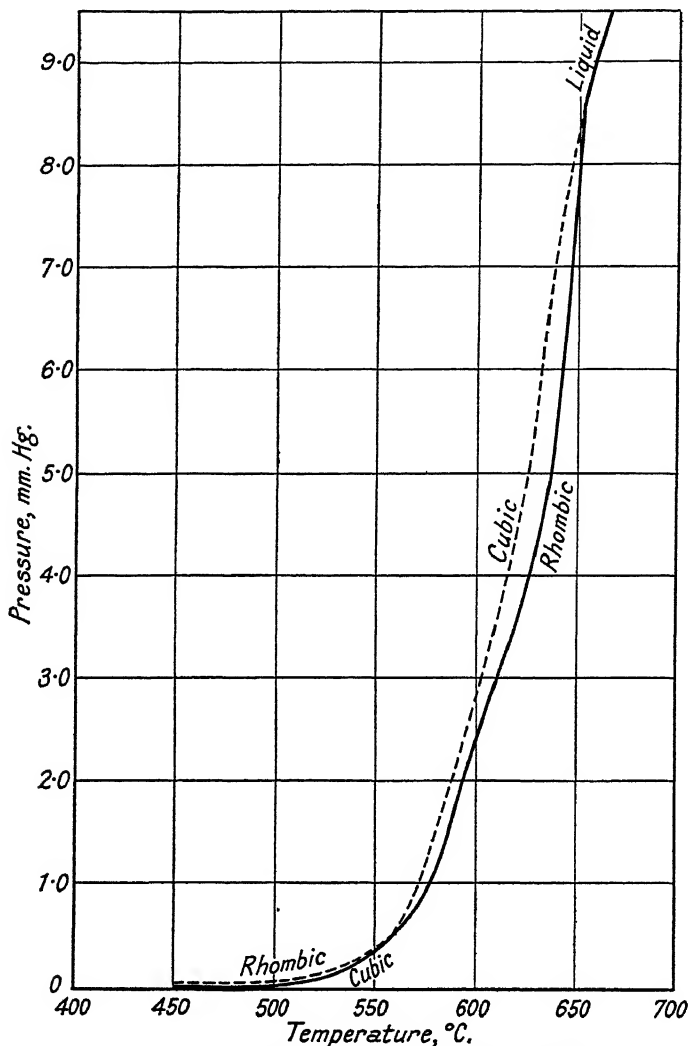


FIG. 2.—Vapour Pressure Curve of Antimony Trioxide.

be Sb_4O_6)¹ is 29,490 gram-calories. The vapour pressure (in millimetres) below the melting point is given by

$$\log p = 12.195 - \frac{10,357}{T}$$

The dielectric constant² is 12.8, and is not affected by high field strengths.³

¹ Hincke, *loc. cit.*

² Günther-Schulze and Keller, *Zeitsch. Physik*, 1932, 75, 78.

³ Günther-Schulze and Betz, *ibid.*, 1931, 71, 106.

VAPOUR PRESSURE OF ANTIMONY TRIOXIDE.

Temperature, ° C.	Pressure (mm. Mercury).	Modification of Sb ₂ O ₃ .
450	0.010	Rhombic (metastable)
450	0.0075	Cubic (stable)
475	0.0224	"
500	0.0625	"
550	0.406	"
557	0.525	Cubic and rhombic (stable)
575	0.908	Rhombic (stable)
600	2.42	"
625	3.91	"
642	7.43	Cubic (metastable)
650	7.60	Rhombic (stable)
655	8.50	"
675	10.42	Liquid
700	13.32	"
750	20.78	"
1456	760	"

Rhombic antimony trioxide, in the form of the mineral valentinite, has the crystallographic axial ratios ¹

$$a : b : c = 0.3910 : 1 : 0.3364$$

The density of the synthetic form ² at 27.4° C. is 5.99; that of the mineral is 5.57. The hardness of the mineral on Mohs' scale is 2.5 to 3.0. The molar heat capacity of the prepared form at low temperatures (assuming the molecule to be Sb₂O₃) is as follows :

Temperature, °C. .	-213.2	-198.3	-182.4	-164.3	-120.7	-92.6	-49.3	-20.1	+1.6	+17.5
Molar heat capacity (gram-calories) .	6.893	9.114	10.97	13.11	16.97	19.05	22.54	22.59	23.57	24.49

The calculated molar latent heat of fusion ³ is 13,250 gram-calories. The vapour pressure (in millimetres) is given by

$$\log p = 11.318 - \frac{9,625}{T}$$

and the molar heat of vaporisation is 22,040 gram-calories. The molar heat of transition from the cubic to the rhombic modification is 1,620 gram-calories.⁴

¹ Laspeyres, *Zeitsch. Kryst.*, 1884, 9, 162; Brezina, *Ann. Museum Wien*, 1886, 1, 145; Groth, *Fogg. Annalen*, 1869, 137, 429.

² Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2712.

³ Hincke, *loc. cit.*

⁴ See also Roberts and Fenwick, *J. Amer. Chem. Soc.*, 1928, 50, 2146.

For other physical properties, see Schuhmann, *J. Amer. Chem. Soc.*, 1924, 46, 52; Grippenberg, *ibid.*, 1911, 33, 1761; Jaeger, *Zeitsch. Kryst. Min.*, 1907, 44, 46; Biltz, *Zeitsch. physikal. Chem.*, 1896, 19, 385; Ditte and Metzner, *Compt. rend.*, 1892, 115, 936; Rideal, *Ber.*, 1886, 19, 589; Guntz, *Compt. rend.*, 1886, 98, 589; Hensgen, *Rec. Trav. chim.*, 1885, 4, 401; Grosse-Bohle, *Zeitsch. Kryst.*, 1881, 5, 222; Meyer and Mensching,

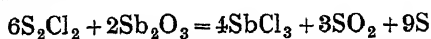
Antimony trioxide, when heated in air, undergoes no change at temperatures below 360°C . Above that temperature it absorbs oxygen¹ and is converted into the tetroxide. At a higher temperature the tetroxide dissociates into trioxide and oxygen; the dissociation begins at about 900°C . and is complete at $1,080^{\circ}\text{C}$.

Antimony trioxide is almost insoluble in both hot and cold water, and also in dilute nitric and sulphuric acids; it will dissolve in dilute hydrochloric acid.² It is oxidised by concentrated nitric acid, a mixture of oxides being formed in which antimony pentoxide predominates.³ With concentrated sulphuric acid, antimony sulphate is formed.⁴ The trioxide is soluble in alkaline solutions, forming antimonites;⁵ it is also soluble in tartaric acid,⁶ in lactic acid,⁷ and in certain other organic compounds.⁸ The statement that antimony trioxide is oxidised when boiled with aqueous alcohol⁹ has been contradicted.¹⁰

At a red heat antimony trioxide is reduced by hydrogen; reduction also occurs on treatment with hydrogen under the influence of the silent electric discharge.¹¹ Hydrogen peroxide is without action.

A complex reaction occurs when the oxide is heated with chlorine, antimony tri- and penta-chlorides being formed in addition to antimony tetroxide. The last is decomposed on further treatment with chlorine.¹²

When antimony trioxide is melted with a little sulphur, a mixture of antimony trisulphide and antimony trioxide, known as "antimony glass," is obtained; with excess of sulphur, antimony trisulphide and sulphur dioxide are formed. A reaction also occurs between antimony trioxide and antimony trisulphide resulting in the formation of metallic antimony.¹³ Thermal investigation of the system $\text{Sb}_2\text{O}_3\text{-Sb}_2\text{S}_3$ indicates the formation of a compound $\text{Sb}_2\text{O}_3 \cdot 5\text{Sb}_2\text{S}_3$ or Sb_4OS_5 (fig. 4).¹⁴ When a current of hydrogen sulphide is passed over the trioxide a yellow coloration is produced in the cold; when heated an oxysulphide is obtained.¹⁵ With ammonium sulphide the trioxide reacts with the formation first of an orange-coloured oxysulphide which passes ultimately into the trisulphide. With sulphur monochloride, antimony trichloride is obtained:¹⁶



Ber., 1879, 12, 1282; Groth, *Pogg. Annalen*, 1869, 137, 426; Fizeau, *Ann. Chim. Phys.*, 1866, [4], 8, 360; Playfair and Joule, *J. Chem. Soc.*, 1846, 3, 83; Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 362; Karsten, *Schweigger's J.*, 1832, 65, 394; Boullay, *Ann. Chim. Phys.*, 1830, [2], 43, 266.

¹ Carnelley and Walker, *J. Chem. Soc.*, 1888, 53, 86; Shakhov and Slobodska, *loc. cit.*

² Terrell, *Ann. Chim. Phys.*, 1866, [4], 7, 380.

³ Péligot, *Compt. rend.*, 1846, 23, 709.

⁴ Schultz-Sellack, *Ber.*, 1871, 4, 13.

⁵ Mitscherlich, *J. prakt. Chem.*, 1840, 19, 455; Cormimbœuf, *Compt. rend.*, 1892, 115, 1305.

⁶ Schulze, *J. prakt. Chem.*, 1883, [2], 27, 322.

⁷ Kretschmar, *Chem. Zeit.*, 1888, 943; Waite, *Techn. Jahresber.*, 1887, 1161.

⁸ Vogel, *Ber.*, 1885, 18, 38; Henderson and Prentice, *J. Chem. Soc.*, 1895, 67, 1030; 1902, 81, 658; Rosenheim and Bierbrauer, *Zeitsch. anorg. Chem.*, 1899, 20, 281; Jordis, *Zeitsch. angew. Chem.*, 1902, 15, 906; Köhler, *Dingl. poly. J.*, 1885, 258, 520.

⁹ Tingle, *J. Amer. Chem. Soc.*, 1911, 33, 1762.

¹⁰ Edgerton, *ibid.*, 1913, 35, 1769.

¹¹ Miyamoto, *J. Chem. Soc. Japan*, 1932, 53, 788.

¹² Weber, *Pogg. Annalen*, 1861, 112, 625; Willgerodt, *J. prakt. Chem.*, 1885, 31, 539.

¹³ Schoeller, *J. Soc. Chem. Ind.*, 1914, 33, 169; 1915, 34, 6; see also Milbauer, *Chem. Zeit.*, 1916, 40, 108.

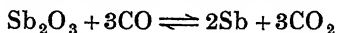
¹⁴ *International Critical Tables*, 1928, 4, 46; Quercigh, *Atti R. Accad. Lincei*, 1912, 21, 415.

¹⁵ Schumann, *Annalen*, 1877, 187, 312.

¹⁶ Oddo and Serra, *Gazzetta*, 1899, 29, II, 355; Prinz, *Annalen*, 1884, 223, 356.

Phosphorus trichloride is decomposed by antimony trioxide with the formation of red phosphorus.¹ The oxide dissolves slightly in phosphoric acid, some phosphate being formed.

The trioxide is reduced when heated with carbon and certain carbon compounds such as carbon monoxide, potassium cyanide, sodium formate, etc.² From an examination of the equilibrium conditions of the reduction by carbon monoxide, according to the equation



between 502° and 596° C. the change in free energy ³ is given by

$$\Delta F = -33,461 + 34.286T \log T - 0.01110T^2 + 0.0000093T^3 - 88.65T$$

Reduction of the trioxide is complete at 500° C.⁴

Antimony trioxide reacts also with silicon tetrachloride ⁵ forming antimony trichloride and silicon; and with silicochloroform ⁶ in the presence of sodium hydroxide, in which case metallic antimony and hydrated silica are obtained. It may be reduced to metal by the action of boron nitride.⁷

The more active metals such as potassium, magnesium and aluminium act as reducing agents; fusion with alkali nitrates results in the formation of antimonates. When fused with caustic soda and sulphur a mixture of antimonate and thioantimonate is formed,⁸ but fusion with sodium hydroxide and arsenic leads to reduction to the metal.⁹

The heat of formation of cubic antimony trioxide ¹⁰ is $149,690 \pm 200$ gram-calories per mole.

Hydrated Antimony Trioxide has not been obtained by direct methods, but three substances, obtained by indirect methods, have been described as *ortho*-, *pyro*- and *meta*-antimonious acids, respectively, with the formulæ H_3SbO_3 , $\text{H}_4\text{Sb}_2\text{O}_5$ and HSbO_2 . The first, which may also be regarded as antimony hydroxide, is obtained by the action of dilute sulphuric acid on a double tartrate of antimony and barium.¹¹ The substance, formerly known as pyro-antimonious acid, which is obtained when antimony trisulphide is heated with a solution of potassium hydroxide, and copper sulphate then added to the mixture,¹² was subsequently ¹³ shown to be *ortho*-antimonic acid, H_3SbO_4 . The substance described as *meta*-antimonious acid, HSbO_2 , is obtained by the decomposition of a double tartrate of potassium and antimony, using an alkali carbonate, phosphate or acetate.¹⁴

There is, however, no conclusive evidence for the existence of these hydrated forms of antimony trioxide. No evidence for the existence

¹ Michaëlis, *J. prakt. Chem.*, 1871, [2], 4, 449; *Bull. Soc. chim.*, 1872, [1], 17, 205.

² Nelissen, *Bull. Acad. roy. Belg.*, 1887, [3], 13, 258.

³ Watanabe, *Bull. Inst. Phys. Chem. Research, Tokyo*, 1929, 8, 973.

⁴ Watanabe, *Sci. Rep. Imp. Univ. Tohoku*, 1933, 22, 407.

⁵ Rauter, *Annalen*, 1892, 270, 251.

⁶ Ruff and Albert, *Ber.*, 1905, 38, 2234.

⁷ Moser and Eidmann, *Ber.*, 1902, 35, 535.

⁸ Mitscherlich, *J. prakt. Chem.*, 1840, 19, 455. See also Factor, *Pharm. Post*, 1905, 38, 527; Brett, *Phil. Mag.*, 1837, [3], 10, 97.

⁹ Kirsebom, *French Patent*, 1930, 694283.

¹⁰ Roberts and Fenwick, *loc. cit.* See also Mixer, *Amer. J. Sci.*, 1909, [4], 28, 103.

¹¹ Clarke and Stallo, *Ber.*, 1880, 13, 1787; Guntz, *Compt. rend.*, 1886, 102, 1472; Carnelley and Walker, *J. Chem. Soc.*, 1888, 53, 60.

¹² Schaffner, *Annalen*, 1844, 51, 182.

¹³ Serono, *Gazzetta*, 1894, 24, II, 274.

¹⁴ Long, *J. Amer. Chem. Soc.*, 1895, 17, 87.

of definite hydrates has been obtained from dehydration curves,¹ and it seems probable that the various substances described are colloidal modifications of hydrated antimony trioxide differing in fineness of division.²

Antimonites.—Antimony trioxide is amphoteric, its basic properties being the more highly developed. Most antimony salts derived from this oxide are, however, hydrolysed by cold water, the exceptions being the trifluoride and some salts of organic acids. Its acidic properties are shown by the formation of antimonites by the action of solutions of alkali and possibly of alkaline earth hydroxides. These are mainly meta-antimonites, derived from the hypothetical acid HSbO_2 ; but other more complex substances have been obtained.

Sodium meta-antimonite, NaSbO_2 , may be taken as typical. It is obtained by fusing together antimony trioxide and excess of sodium carbonate;³ a trihydrate has also been obtained.⁴ It is oxidised by fusion with caustic soda in contact with air, by hydrogen peroxide, and by the halogens.⁵ By treatment with hydrogen sulphide a thioantimonite is formed;⁶ and with sodium thiosulphate a mixture of sodium pyroantimonate and thioantimonate is formed, the thiosulphate being reduced to sulphite.⁷ In solution the sodium salt reacts with solutions of many metallic salts. With copper salts it yields a precipitate, probably of copper antimonite, soluble in nitric acid.⁸ With an ammoniacal solution of barium chloride, with solutions of mercurous salts, mercuric chloride and lead and ferric salts precipitates are formed in each case, while with ferric salts a reddish solution is ultimately formed. With silver nitrate a complex reaction occurs yielding a black precipitate, which is a mixture of silver oxide, silver and antimony;⁹ while with gold chloride a black precipitate is obtained which is possibly gold antimonite.¹⁰

A solution of sodium antimonite is reduced by stannous chloride, and is oxidised by potassium permanganate, potassium dichromate or potassium ferricyanide.¹¹

Other, and in many cases more complex, antimonites that have been formed include the sodium salt NaSb_3O_5 , which is obtained by the prolonged boiling of a mixture of excess of antimony trioxide and a solution of sodium hydroxide,¹² and the salt $\text{Na}_2\text{Sb}_4\text{O}_7$. A potassium salt of indefinite composition has been described by a number of the early observers.¹³ The two salts KSb_3O_5 and $\text{K}_2\text{Sb}_{16}\text{O}_{25} \cdot 7\text{H}_2\text{O}$ have

¹ Simon and Poehlmann, *Zeitsch. anorg. Chem.*, 1925, 149, 101.

² See also Lea and Wood, *J. Chem. Soc.*, 1923, 123, 259; Mitscherlich, *J. prakt. Chem.*, 1840, 19, 445.

³ Mitscherlich, *J. prakt. Chem.*, 1840, [1], 19, 455.

⁴ Terreil, *Ann. Chim. Phys.*, 1866, [4], 7, 352; Cormimbœuf, *Compt. rend.*, 1892, 115, 1306.

⁵ Rose, *Pogg. Annalen*, 1824, 3, 441; Frémy, *Ann. Chim. Phys.*, 1848, [3], 23, 404; *J. prakt. Chem.*, 1848, [1], 45, 209; Mitscherlich, *loc. cit.*; Hager, *Zeitsch. anal. Chem.*, 1872, 11, 82.

⁶ Terreil, *loc. cit.*

⁷ Weinland and Gutmann, *Zeitsch. anorg. Chem.*, 1898, 17, 413.

⁸ Terreil, *loc. cit.*; Harding, *Zeitsch. anorg. Chem.*, 1899, 20, 235.

⁹ Pillitz, *Zeitsch. anal. Chem.*, 1882, 21, 27, 496; see also Terreil, *loc. cit.*; Rose, *loc. cit.*; Bunsen, *Annalen*, 1858, 106, 1.

¹⁰ Harding, *loc. cit.*; Rose, *loc. cit.*

¹¹ Quinke, *Zeitsch. anal. Chem.*, 1892, 31, 35.

¹² Cormimbœuf, *loc. cit.*; Terreil, *loc. cit.*

¹³ Berzelius, *Schweigger's J.*, 1812, 6, 144; Brandes, *ibid.*, 1831, 62, 199; Rose and Varrentrapp, *Pogg. Annalen*, 1839, 47, 326; von Liebig, Poggendorff and Wöhler, "*Handwörterbuch der reinen und angewandten Chemie*" (Braunschweig), 1837, 1, 414.

been obtained, the former as minute, prismatic crystals.¹ Antimonites of copper have been obtained by a fusion method,² while the mineral *thrombolite* probably also contains a compound of this type.³ Antimonites of the alkaline earth metals have not been isolated, but indications of their existence have been obtained,⁴ while the mineral *romeite* may contain an antimonite of calcium.⁵ Antimonites of zinc, magnesium and lead,⁶ and of iron, cobalt and nickel,⁷ have been obtained. In addition, complex compounds of antimony trioxide and alkali molybdates and tungstates have been described.⁸ Of the tungstates, the following may perhaps be mentioned:⁹ $2\text{BaO} \cdot \text{Sb}_2\text{O}_3 \cdot 11\text{WO}_3 \cdot 18\text{H}_2\text{O}$; $6(\text{NH}_4)_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 38\text{H}_2\text{O}$; $6(\text{CH}_3\text{N}_3)_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 31\text{H}_2\text{O}$; $8\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 19\text{WO}_3 \cdot 37\text{H}_2\text{O}$; $2\frac{1}{2}(\text{NH}_4)_2\text{O} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 12\text{H}_2\text{O}$; $3\text{K}_2\text{O} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 6\text{H}_2\text{O}$; $2\frac{1}{2}(\text{CH}_3\text{N}_3)_2\text{O} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 6\text{H}_2\text{O}$; $2\frac{1}{2}\text{BaO} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 18\text{H}_2\text{O}$.

Antimony trioxide is used under various trade names, such as "Luv extra," "Leukonin" and "Timonox," as an opacifier mixed with paints. The commercial product is usually a mixture of oxides. It can be used with all colours and oxides except those containing lead. The durability, hardness and speed of drying of antimony white paints are stated to be less than for zinc white paints.¹⁰ The trioxide is also employed in enamels, but certain countries have introduced legislation curtailing its use on food receptacles on account of its poisonous nature. It has been shown that whilst antimony in the quinquivalent form is comparatively harmless, it is poisonous in the tervalent form since it is then soluble in dilute acids¹¹ (see p. 46).

Antimony Tetroxide, Sb_2O_4 , or Antimony Dioxide, SbO_2 , is found naturally as the mineral *cervantite*. It may be obtained by a variety of methods, such as by the prolonged heating of antimony trioxide in air, or by the calcination of antimony pentoxide,¹² or by heating the trioxide with excess of mercuric oxide.¹³ It is usually prepared by heating antimony or antimony trisulphide with nitric acid and igniting the residue at a dull red heat until the weight is constant.¹⁴ An impure form may be obtained by the careful roasting of antimony trisulphide, at a temperature below the melting point, until no more sulphur dioxide is evolved.¹⁵

¹ Cormimbœuf, *loc. cit.*

² Tammann, *Zeitsch. anorg. Chem.*, 1925, 149, 68; 1927, 160, 101; Balareff, *ibid.*, 1927, 160, 92.

³ Breithaupt, *J. prakt. Chem.*, 1838, [1], 15, 320; Schrauf, *Zeitsch. Kryst.*, 1880, 4, 28; Domeyko, "*Elementos de Mineralogia*" (Santiago), 1871.

⁴ Tammann, *loc. cit.*; Balareff, *loc. cit.*

⁵ Damour, *Ann. Mines*, 1841, [3], 20, 247; Groth, "*Tabellarische Uebersicht der Mineralien*" (Braunschweig), 1889, 71; Schaller, *Bull. U.S. Geol. Survey*, 1916, 610; Pelloux, *Ann. Mus. Storia Nat. Geneva*, 1913, [3], 6, 22; Schroder, "*Goldschmidt's Atlas der Kristallformen*," 1913, 1, 121; Hussak, *Centr. Min.*, 1905, 240.

⁶ Tammann, *loc. cit.*; Balareff, *loc. cit.*

⁷ Berzelius, *loc. cit.*; Tammann, *loc. cit.*; Balareff, *loc. cit.*

⁸ Gibbs, *Amer. Chem. J.*, 1885, 7, 313, 392.

⁹ Rosenheim and Wolff, *Zeitsch. anorg. Chem.*, 1930, 193, 64.

¹⁰ Müller, *Glashütte*, 1932, 62, 320; Riker, *Amer. Paint J.*, 1933, 17, No. 39, 47; Kolke, *Farben Zeitung*, 1933, 38, 676; Haupt and Popp, *Keram. Rundschau*, 1927, 35, 221; van Hoek, *Farben Zeitung*, 1932, 37, 1222, 1255; 38, 43, 1749.

¹¹ Melzer, *Glashütte*, 1929, 59, 865; Haupt and Popp, *loc. cit.*; Kolke, *loc. cit.*

¹² Berzelius, *Schweigger's J.*, 1812, 6, 144.

¹³ Bunsen, *Annalen*, 1878, 192, 315.

¹⁴ von Szilágyi, *Zeitsch. anal. Chem.*, 1918, 57, 23; Dexter, *Pogg. Annalen*, 1857, 100, 563; Bunsen, *loc. cit.*

¹⁵ Capitaine, *J. Pharm. Chim.*, 1839, [3], 25, 516.

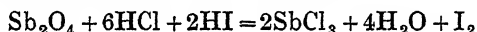
Antimony tetroxide is a refractory, white powder, massive as a mineral; it becomes yellowish on heating, reverting to white when cold. The crystal lattice is cubic,¹ with $a = 10.22$ Å. The density of the synthetic substance² at 23.8° C. is given as 6.47. This value is considerably higher than that given for the mineral (see p. 9). The specific heat is 0.0951;³ the molar heat capacity at low temperatures is given in the following table (in gram-calories per mole):⁴

Temp., ° C.	-200.2	-182.4	-150.4	-129.2	-79.3	-72.1	-16.6	-1.1	+11.9
Heat capacity.	8.317	10.02	14.72	16.57	21.37	21.74	25.23	26.10	27.17

The tetroxide is stable at a red heat, but loses oxygen when heated more strongly.⁵

The crystal structure of antimony tetroxide suggests that the antimony atoms are not all equivalent,⁶ and from a comparison with the structure of the similarly constituted antimonates of lead and calcium it is suggested that the oxide may be antimony antimonate, $\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{O}_4$.

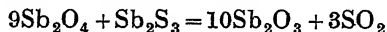
Antimony tetroxide is soluble with great difficulty in water and in acids. It is slightly acidic, imparting a faint reddish colour to moistened litmus.⁷ It is only slightly attacked when heated with hydrochloric acid, but dissolves in hydrochloric acid containing hydriodic acid, with liberation of iodine, according to the equation



This reaction may be employed for the estimation of antimony tetroxide.⁸

When heated with a little sulphur an oxysulphide or "antimony glass" is formed; with more sulphur the trisulphide is obtained.⁹ Alkali hydrosulphides have no action in the cold, but when warmed they act as solvents, hydrogen sulphide being evolved.

The tetroxide can be reduced to the metal by heating with carbon, potassium cyanide or the alkali metals; the trioxide is obtained on heating with antimony. The tetroxide will also react with antimony trisulphide: when excess of the tetroxide is employed the trioxide is formed with liberation of sulphur dioxide:



With excess of the sulphide, "antimony glass" is formed.

The heat of formation from the elements¹⁰ is 209,800 gram-calories.

A hydrated form, $\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$ or $\text{H}_2\text{Sb}_2\text{O}_5$, is found in the mineral *stibicomite*. It is acidic, and the free acid, *meta-hypoantimonic acid*, may

¹ Dehlinger, *Zeitsch. Krist.*, 1927, 66, 108.

² Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2712. See also Karston, *Schweigger's J.*, 1832, 65, 394; Playfair and Joule, *Memoirs Chem. Soc.*, 1845, 2, 401.

³ Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129; *Pogg. Annalen*, 1841, 53, 73.

⁴ Anderson, *loc. cit.*

⁵ Foote and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1344; Dexter, *loc. cit.*; Baubigny, *Compt. rend.*, 1897, 124, 560; Brunck, *Zeitsch. anal. Chem.*, 1895, 34, 171; Read, *J. Chem. Soc.*, 1894, 65, 313; Carnelley and Walker, *ibid.*, 1888, 53, 86; Guntz, *Compt. rend.*, 1885, 101, 161.

⁶ Natta and Baccaredda, *Zeitsch. Krist.*, 1933, 85, 271.

⁷ Rose, *Pogg. Annalen*, 1824, 3, 441.

⁸ von Szilágyi, *loc. cit.*

⁹ Proust, *Gehlen's allg. J. Chem.*, 1805, 5, 543; *Gilbert's Annalen*, 1807, 25, 186.

¹⁰ Mixer, *Amer. J. Science*, 1909, [4], 28, 103.

be prepared as a white, flocculent powder by decomposing solutions of its salts by acids. The potassium salt may be obtained by heating antimony or antimony trisulphide with potassium sulphate or bisulphate; other salts may be prepared by double decomposition. It has been suggested, however, that these salts are mixtures of antimonites and antimonates.¹

Antimony Pentoxide, Sb_2O_5 .—Antimony pentoxide and its derivatives were employed in the sixteenth and seventeenth centuries as diaphoretics.² A potassium salt was described by Basil Valentine by the name of "*antimonium diaphoreticum ablutum*"; it was prepared by deflagrating a mixture of antimony and saltpetre and washing the residue with water and alcohol. A similar substance was "*antimonium diaphoreticum non ablutum*." The acid, or oxide, was probably obtained by the action of acids upon the above substances, and was used medicinally under the name of "*materia perlata Kerkringii*." Glauber obtained a similar product, which he called "*benzoardicum minerale*," by the action of nitric acid upon antimony trichloride.³

Antimony pentoxide may be prepared by heating antimony, or a lower oxide of antimony, with nitric acid or aqua regia.⁴ It may also be obtained by ignition of the hydrated pentoxide (antimonic acid), which may, in its turn, be prepared by the hydrolysis of antimony pentachloride. It is formed in a variety of reactions, many of which, however, are not suitable for its preparation. Among these reactions may be mentioned the action of alkaline hydrogen peroxide upon antimony⁵ or antimony trioxide;⁶ and the deflagration of a mixture of antimony, antimony trioxide, antimony trisulphide or potassium antimonyl tartrate with potassium nitrate.

Antimony pentoxide is a pale, lemon-yellow powder, without taste. Its density is 3.78. It crystallises in the cubic system, with a lattice constant similar to that of the tetroxide.⁷ The arrangement of the oxygen atoms in the lattice, and the effect of adding oxygen atoms within the range Sb_2O_4 to Sb_2O_5 , affords a possible explanation for the development of colour in the neighbourhood of Sb_2O_{13} .⁸ The pentoxide is insoluble in alcohol, but soluble in tartaric acid.⁹

The heat of formation, calculated from thermal data obtained in the

¹ For the chemical properties of antimony tetroxide, see also Berzelius, *Schweigger's J.*, 1812, 6, 144; 1818, 22, 69; Delffs, *J. prakt. Chem.*, 1847, 40, 318; Schnabel, *Pogg. Annalen*, 1858, 105, 146; Cumenge, *Ann. Mines*, 1851, [4], 20, 80; Frenzel, *Zeitsch. Kryst. Min.*, 1877, 2, 629; Santos, *Chem. News*, 1877, 36, 167; Rammelsberg, "*Handwörterbuch des chemischen Theils der Mineralogie*" (Leipzig), 1875, 175, 188; Frémy, *Ann. Chim. Phys.*, 1844, [3], 12, 498; von Liebig, *loc. cit.*, 1, 414; Websky, *Zeitsch. anal. Chem.*, 1872, 11, 124.

² A diaphoretic is used for promoting or increasing perspiration.

³ Dyson, *Pharmaceutical J. and Pharmacist*, 1928, [4], 67, 521; Kopp, "*Geschichte der Chemie*" (Braunschweig), 1843–1847, 4, 108; Libavius, "*Alchymia*" (Frankfurt), 1595; Lemery, "*Cours de Chimie*" (Paris), 1675; Basil Valentine, "*The Triumphant Chariot of Antimony*," London, 1661; Croll, "*Basilica chymica*" (Frankfurt), 1609; Glauber, "*Pharmacopœa spagyrica*" (Amstelodani), 1650–1670.

⁴ Berzelius, *loc. cit.*; Bourson, *J. prakt. Chem.*, 1839, 17, 238; Conrad, *Chem. News*, 1879, 40, 197; Bosek, *J. Chem. Soc.*, 1895, 67, 515; Millon, *Ann. Chim. Phys.*, 1842, [3], 6, 101; Rose, *Pogg. Annalen*, 1841, 53, 161; Lefort, *J. Pharm. Chim.*, 1855, [3], 28, 93.

⁵ Clark, *Chem. News*, 1893, 67, 249.

⁶ Zambelli and Luzzatto, *Arch. Pharm.*, 1886, [2], 224, 772; Hampe, *Chem. Zeit.*, 1894, 18, 1899.

⁷ Dehlinger, *Zeitsch. Krist.*, 1927, 66, 108.

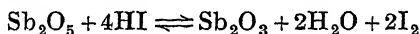
⁸ Dehlinger, *Zeitsch. physikal. Chem.*, 1929, 6 B, 127.

⁹ Playfair and Joule, *Memoirs Chem. Soc.*, 1845, 2, 401; Boullay, *Ann. Chim. Phys.*, 1830, [2], 43, 266.

oxidation of the element or lower oxides by means of sodium peroxide,¹ is 229,600 gram-calories. The molar heat capacity at low temperatures (in gram-calories per mole) calculated from determinations of specific heat on two hydrated forms² is given in the following table :

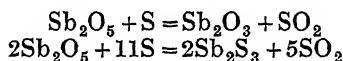
Temperature, °C. .	-213	-203	-173	-123	-103	-73	-3	+17	+27
Heat capacity .	5.75	7.83	12.66	18.46	20.32	22.67	26.54	27.62	28.23

The pentoxide is decomposed on heating, decomposition beginning at about 300° C. with the formation of antimony tetroxide,³ and also by hydrogen under the influence of the silent electric discharge.⁴ With chlorine it forms antimony trichloride ;⁵ hydrochloric acid has a slight solvent action, but no chlorine is evolved. It is reduced by phosphorus trichloride.⁶ Hydriodic acid reduces it to antimony trioxide with liberation of iodine.⁷ This reaction affords a delicate qualitative test for antimony.⁸ The reaction

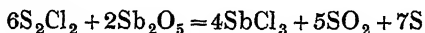


is reversible, and the equilibrium conditions have been studied with reference to the influence of varying concentrations of the reacting substances and of the presence of certain other substances.⁹ Reduction of the antimony pentoxide is practically complete in the presence of excess of potassium iodide or hydrochloric acid, the latter being the more effective. The presence of tartaric acid reduces the amount of iodine set free ; cadmium iodide acts similarly ; but the presence of neutral salts, or a rise in temperature, increases the amount.

Antimony pentoxide reacts with sulphur to form antimony trioxide, or antimony trisulphide, according to the proportion of sulphur,¹⁰ the reactions being represented by the following equations :



When heated in a current of hydrogen sulphide a black oxysulphide, Sb_4OS_5 , is formed ;¹¹ an orange-red precipitate of antimony penta-sulphide is obtained with a solution of hydrogen sulphide. This precipitate is soluble in warm alkali sulphides, and very slowly soluble in ammonium sulphide. Sulphuric acid, both dilute and concentrated, dissolves antimony pentoxide only slowly and after prolonged action. The pentoxide reacts with sulphur monochloride¹² with the formation of antimony trichloride :



¹ Mixer, *Amer. J. Sci.*, 1909, [4], 28, 103.

² Anderson, *loc. cit.*

³ Daubrowa, *Annalen*, 1877, 186, 118.

⁴ Miyamoto, *J. Chem. Soc. Japan*, 1932, 53, 788.

⁵ Weber, *Pogg. Annalen*, 1861, 112, 625.

⁶ Michaelis, *J. prakt. Chem.*, 1871, 4, 454.

⁷ Bunsen, *Annalen*, 1858, 106, 1.

⁸ Klein, *Arch. Pharm.*, 1889, 227, 922; Giraud, *Bull. Soc. chim.*, 1886, [2], 46, 504; Gooch and Gruener, *Zeitsch. anal. Chem.*, 1893, 32, 471; Weller, *Annalen*, 1882, 213, 364; Herroun, *Chem. News*, 1882, 45, 101; Rohrer, *Ber.*, 1901, 34, 1565.

⁹ Kolb and Formhals, *Zeitsch. anorg. Chem.*, 1908, 58, 189. See also Youtz, *Zeitsch. anorg. Chem.*, 1903, 37, 337.

¹⁰ Rammelsberg, *Pogg. Annalen*, 1841, 52, 241.

¹¹ Schumann, *Annalen*, 1877, 187, 312.

¹² Prinz, *Annalen*, 1884, 223, 358.

Antimony pentoxide is partially reduced when heated with carbon in the blowpipe flame, but for complete reduction admixture with sodium carbonate is necessary. Carbon disulphide¹ and silicon tetrachloride² also act as reducing agents, chlorine being evolved in the latter case.

Aqueous alkali solutions have only a slight solvent action, but antimonates are formed on fusion with alkalis. Reduction occurs on fusion with potassium cyanide, potassium formate, the sulphides of lead, copper and silver,³ antimony and antimony trisulphide.

Antimony pentoxide liberates chlorine from potassium chloride⁴ and iodine from potassium iodide,⁵ in both cases on heating in the presence of oxygen.

Stannous chloride produces a darkening of the colour of antimony pentoxide, the resulting product containing stannous oxide.⁶ The pentoxide is reduced to antimony by the action of tin and hydrochloric acid.⁷

The hydration of antimony pentoxide has been studied by many investigators, and, while earlier workers reported a number of definite hydrates, more recent work suggests that the hydrates of antimony pentoxide resemble those of stannic oxide in being colloidal. Three of the so-called hydrates have been studied, being prepared respectively by (1) the hydrolysis of antimony pentachloride at 0° to 1° C., (2) the hydrolysis of antimony pentachloride at 100° C., and (3) the oxidation of antimony trichloride by nitric acid and hydrolysis of the product at 60° C. The results suggested that gels were formed in each case, the behaviour of these depending upon grain size, this in turn varying with the method of preparation. The three products contained the following molecules of water per molecule of antimony pentoxide after treatment as described :⁸

	(1)	(2)	(3)
Dried on porous plate . . .	30.57	9.97	7.91
Dried over sulphuric acid . . .	3.68	2.17	0.60
Dried at 105° C.	2.43	1.02	0.45

Alcogels of antimony pentoxide have also been prepared, and their de-alcoholation curves were found to be similar.

Sols have been obtained⁹ by the hydrolysis of concentrated aqueous solutions of antimony pentachloride at 0° C. Freezing point determinations of these solutions suggest analogies with soap solutions, while pH values indicate that, on subsequent dilution, the micelles decompose further and ionise. Certain of the more stable solutions suggest a molecular weight of a very high order. The soluble products are acidic, and are probably hydrosols of low stability. It is probable that the ortho-, pyro- and meta-antimonic acids have no free existence. Towards alkalis, these hydrates show marked selective adsorption, forming amorphous substances, probably antimonates, of indefinite composition.

¹ Müller, *Pogg. Annalen*, 1866, 127, 404.

² Rauter, *Annalen*, 1892, 270, 250.

³ Rammelsberg, *loc. cit.*

⁴ Schulze, *J. prakt. Chem.*, 1880, 21, 437.

⁵ Schönbein, *Pogg. Annalen*, 1849, 78, 513.

⁶ Schiff, *Annalen*, 1861, 120, 55.

⁷ Mengin, *Compt. rend.*, 1894, 119, 224.

⁸ Jander and Simon, *Zeitsch. anorg. Chem.*, 1923, 127, 68.

⁹ Glizelli and (Mlle.) Deniszczukowna, *Compt. rend.*, 1926, 182, 521.

Certain crystalline antimonates may also be obtained by dissolution in concentrated alkali solutions, followed by careful evaporation at low temperature.¹

Evidence has been obtained for the existence of the definite hydrate $3\text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ from a study of the behaviour of gels obtained by the hydrolysis of antimony pentachloride,² and also for the existence of a dihydrate and a hemihydrate. The formula $\text{HSb}(\text{OH})_6$ has also been suggested for antimonous acid.³ Earlier investigators have described several hydrates obtained by the following methods: by the decomposition of a solution of potassium antimonate by nitric acid;⁴ by the hydrolysis of antimony pentachloride;⁵ by the repeated action of aqua regia on antimony;⁶ by the action of nitric acid upon antimony trichloride.⁷

Much confusion exists as to the nature of the many antimonates that have been obtained and described. It seems fairly certain that only in a few instances—notably the salts of iron and aluminium—are normal ortho-antimonates obtained, the majority of the salts being either acid ortho-antimonates of the type KH_2SbO_4 , or meta-antimonates of the type KSbO_3 . The elucidation of the constitution of these salts is handicapped by the difficulty experienced in determining the true water content of the solid substances. From conductivity determinations in solution it appears probable that both the potassium and the sodium salts are acid ortho-antimonates of the above type.⁸ The following compounds have been obtained by the interaction of a concentrated solution of a salt of the metal with a concentrated solution of sodium antimonate:—⁹

Ortho-antimonates— $\text{Fe}_2\text{O}_3 \cdot \text{Sb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$; $\text{Al}_2\text{O}_3 \cdot \text{Sb}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$.

Meta-antimonates— $\text{CuSb}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$; $\text{Ag}_3\text{Sb}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$; $\text{BeSb}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$; $\text{BaSb}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$; $\text{ZnSb}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$; $\text{CdSb}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$; $\text{PbSb}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$; $\text{MnSb}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$; $\text{NiSb}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$; $\text{CoSb}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$. The last two have also been obtained with 12 molecules of water of hydration.¹⁰

In many cases the proportion of water retained in the molecule depends upon the conditions of preparation. In general, this water is

¹ Jander, *Kolloid Zeitsch.*, 1918, 23, 122; Lottermoser, *Zeitsch. Elektrochem.*, 1927, 33, 514.

² Simon and Thaler, *Zeitsch. anorg. Chem.*, 1927, 161, 113.

³ Pauling, *J. Amer. Chem. Soc.*, 1933, 55, 1895; 1933, 55, 3052; Hammett, "Solutions of Electrolytes" (New York), 1929, 108; Brintzinger and Wallach, *Angew. Chem.*, 1934, 47, 61.

⁴ Heffter, *Pogg. Annalen*, 1852, 86, 419.

⁵ Daubrowa, *Annalen*, 1877, 186, 110.

⁶ Conrad, *Chem. News*, 1879, 40, 197.

⁷ Senderens, *Bull. Soc. chim.*, 1899, [3], 21, 47. For the properties of these products, see also Geuther, *J. prakt. Chem.*, 1871, 4, 438; Frémy, *ibid.*, 1848, 45, 211; Baubigny, *Compt. rend.*, 1897, 124, 499; Capitaine, *J. Pharm. Chim.*, 1839, 25, 516; *J. prakt. Chem.*, 1839, 18, 449; Beilstein and von Bläse, *Bull. Acad. St. Petersburg*, 1889, [4], 1, 97, 201, 209; *Chem. Zentr.*, 1889, I, 803; 1890, I, 350; Schiff, *Annalen*, 1857, 102, 111; Luckow, *Zeitsch. anal. Chem.*, 1897, 26, 14; Delacroix, *J. Pharm. Chim.*, 1897, [6], 6, 337; *Bull. Soc. chim.*, 1899, [3], 21, 1049; 1901, 25, 288; Lottermoser, *Zeitsch. Elektrochem.*, 1927, 33, 514.

⁸ Tomula, *Zeitsch. anorg. Chem.*, 1921, 118, 81; Delacroix, *Bull. Soc. chim.*, 1899, [3], 21, 1049; *J. Pharm.*, 1897, [6], 6, 337; Senderens, *Bull. Soc. chim.*, 1899, [3], 21, 47; Baubigny, *Compt. rend.*, 1897, 124, 499; Beilstein and von Bläse, *Chem. Zentr.*, 1889, I, 803; 1890, I, 350; von Knorre and Olschewsky, *Ber.*, 1885, 18, 2353; 1887, 20, 3043; Raschig, *ibid.*, 1885, 18, 2743; Frémy, *Ann. Chim. Phys.*, 1844, [3], 12, 499; 1848, 22, 404.

⁹ Ebel, *Ber.*, 1889, 22, 3044; *Inaug. Dissertation*, Berlin, 1890; *Chem. Zentr.*, 1891, II, 414.

¹⁰ See also Schiff, *Annalen*, 1861, 120, 55; Schneider, *Pogg. Annalen*, 1856, 98, 304; Heffter, *ibid.*, 1852, 86, 418.

removed completely by heating to 100° C. or by drying over concentrated sulphuric acid. In the case of potassium antimonate it is much more difficult to remove the water, and the suggestion has been put forward that in this case a pyro-antimonate may be formed.

Alkali antimonates are to some extent soluble in water, but antimonates of the heavy metals are, in general, soluble only with difficulty. The solubility of sodium meta-antimonate (expressed in milligrams $\text{Na}_2\text{O} \cdot \text{Sb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ in 100 c.c. of solution) is 56.4 in water at 18° C., 0.1 in a mixture of equal volumes of water and ethyl alcohol, and 3.1 in a 2.5 per cent. solution of sodium acetate.¹

Most antimonates are decomposed by concentrated acids with the formation of hydrated antimony pentoxide. Solutions of alkali antimonates react slowly with sulphuretted hydrogen in the absence of other alkali salts, an orange-red precipitate of antimony pentasulphide being formed; they react with carbon dioxide to form a white precipitate of an acid alkali antimonate.²

A number of naturally occurring antimonates has been examined and the constitutions have been discussed.³

ANTIMONY AND SULPHUR.

Three sulphides of antimony have been described: the trisulphide, Sb_2S_3 , the tetrasulphide, Sb_2S_4 , and the pentasulphide, Sb_2S_5 . Some doubt has been expressed concerning the existence of the tetrasulphide as a true compound, and it is probable that the pentasulphide has not yet been obtained in a pure condition. Early investigators described a subsulphide, Sb_2S_2 , obtained by fusion, but this was quickly proved to be a mixture, or solid solution, of antimony and antimony trisulphide.⁴

Thermal examination of the system antimony-sulphur indicates the existence of one compound only—antimony trisulphide, Sb_2S_3 —which gives rise to a maximum on the freezing point curve at 546° C. One eutectic is obtained, containing 57.5 atomic per cent. of sulphur, and melting at 520° C. A second eutectic has been reported, containing 61.3 per cent. sulphur and melting at 519° C. Two liquid layers are obtained at each end of the system, at 530° C. for the sulphur end, and at 615° C. for the antimony end.⁵ (See fig. 3, p. 98.)

Antimony Trisulphide, Sb_2S_3 , has been known from very early times, under a variety of names, such as *antimonium crudum*, *grey antimony ore*, *antimony glance*, *antimony glass*, *stibnite*. Until the eighteenth century it was frequently confused with antimony metal. It exists in at least three forms, a crystalline form and two amorphous forms, each of which may be obtained in a variety of ways.

¹ Tomula, *loc. cit.*

² von Knorre and Olschewsky, *loc. cit.* For further chemical properties of antimonates, see Brunck, *Zeitsch. anal. Chem.*, 1895, 34, 171; Unger, *Arch. Pharm.*, 1871, [2], 147, 193; Rose, *Pogg. Annalen*, 1824, 3, 441; 1848, 73, 582; 1853, 90, 201. For the electrolytic behaviour of solutions of potassium antimonate, see Schmucker, *Zeitsch. anorg. Chem.*, 1894, 5, 199; Smith and Wallace, *ibid.*, 1893, 4, 273.

³ Schaller, *Bull. U.S. Geol. Survey*, 1916, 610, 104. See also Natta and Baccaredda, *Zeitsch. Krist.*, 1933, 85, 271.

⁴ Faraday, *Pogg. Annalen*, 1831, 23, 314; Berzelius, *ibid.*, 1836, 37, 163; Pélabon, *Compt. rend.*, 1904, 138 A, 277; Guinchant and Chrétien, *ibid.*, 1906, 142, 709; Unger, *Arch. Pharm.*, 1871, [2], 147, 199; 1871, [2], 148, 2.

⁵ *International Critical Tables*, 1928, 4, 25; Jaeger and van Klooster, *Zeitsch. anorg. Chem.*, 1912, 78, 245; Guinchant and Chrétien, *Compt. rend.*, 1904, 138, 1269; 1904, 139, 288; 1906, 142, 708; Britzke and Zaetev, *Mineraln. Suvr'e*, 1931, 5, 816.

Crystalline antimony trisulphide may be formed by fusing together the elements ; by subjecting a mixture of the elements to high pressure ;¹ or by heating the elements with water under pressure.² It may also be formed from antimony by the action of sulphur dioxide,³ and from antimony trioxide, or from antimonates, by fusion with sulphur.⁴ It is also obtained by the action of hydrogen sulphide on the vapour of antimony trichloride⁵ or other antimony compounds,⁶ and by the prolonged heating at a high temperature of potassium antimonyl tartrate with a solution of ammonium thiocyanate,⁷ or with potassium thiocyanate⁸ in the presence of tartaric acid. In the latter case the

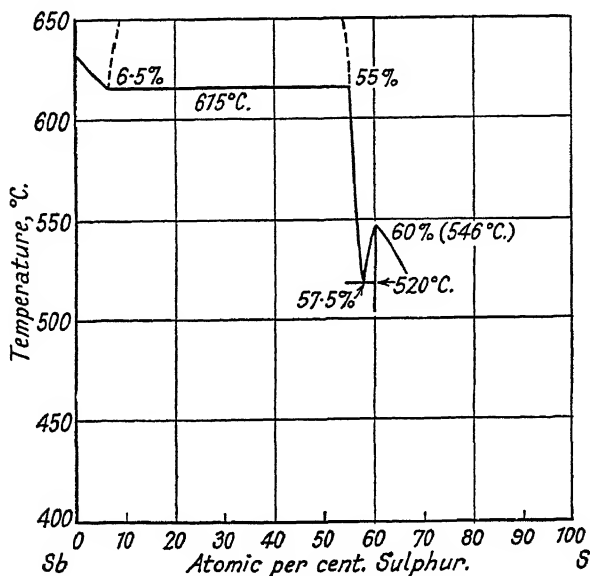


FIG. 3.—Antimony-Sulphur System.

amorphous variety is obtained at lower temperatures, the crystalline at higher.

From antimony pentasulphide the crystalline trisulphide may be obtained by heating at 200° to 300° C. in a current of carbon dioxide ;⁹ by the prolonged action of sunlight on a dilute solution in hydrochloric acid containing hydrogen sulphide ;¹⁰ or by heating in a tube at 250° C. with a solution of sodium bicarbonate.¹¹

¹ Spring, *Ber.*, 1883, 16, 999.

² Geitner, *Annalen*, 1864, 129, 359.

³ Geitner, *loc. cit.*

⁴ Jannasch and Remmler, *Ber.*, 1893, 26, 1425; Unger, *Arch. Pharm.*, 1871, [2], 147, 193.

⁵ Durocher, *Compt. rend.*, 1851, 32, 823; Arctowski, *Zeitsch. anorg. Chem.*, 1895, 8, 220.

⁶ Carnot, *Compt. rend.*, 1879, 89, 169.

⁷ Weinschenk, *Zeitsch. Kryst. Min.*, 1890, 17, 499.

⁸ Warren, *Chem. News*, 1892, 66, 287.

⁹ Rose, "*Handbuch der analytischen Chemie*" (Berlin, 1867-71), 6th Ed., Vol. II, p. 295; Paul, *Zeitsch. anal. Chem.*, 1892, 31, 539.

¹⁰ Brauner, *J. Chem. Soc.*, 1895, 67, 527.

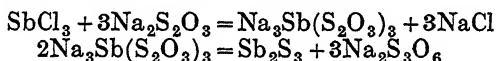
¹¹ de Sénarmont, *Ann. Chim. Phys.*, 1851, [3], 32, 129.

From antimonie solutions the trisulphide is obtained by the action of hydrogen sulphide at 70° C. in the presence of chromic chloride; the presence of the latter is essential for the formation of the black modification of antimony trisulphide in a pure condition.¹ Preparation may also be effected by alternating current electrolysis of sodium thiosulphate solutions using antimony electrodes.²

The amorphous variety may be transformed into the crystalline by heating in a neutral atmosphere;³ by heating with water at 200° to 300° C. in a closed tube,⁴ or by heating with hydrogen sulphide.⁵ The transformation is also effected by the action of dilute acids, especially hydrochloric acid.⁶

Amorphous antimony trisulphide is said to be formed by quenching the molten substance rapidly.⁷ A much purer product is obtained by distilling the trisulphide in a stream of nitrogen and condensing the vapour rapidly; admixed sulphur may be removed by treatment with carbon disulphide.⁸

The amorphous form is also obtained by the action of sodium thiosulphate upon solutions of antimony salts.⁹ The technical product is obtained by this method. A solution of sodium thiosulphate containing sodium hydroxide is added to one of antimony trichloride; the colour of the resulting red product is influenced by the proportion of sodium hydroxide, becoming yellower with increase of this reagent.¹⁰ The reaction may be represented by the equations:



The product is generally contaminated with oxide.

A more usual laboratory method of preparation, however, is by precipitation from solutions of antimony salts by hydrogen sulphide. Tartaric acid should be present to prevent the formation of thio-salts.¹¹ An investigation into the separation of antimony and tin by hydrogen sulphide in hot hydrochloric acid solution indicated that, with a concentration of 30 c.c. concentrated acid in 100 c.c. solution precipitation of antimony trisulphide began at 95° C., that of antimony pentasulphide at 80° C.; the presence of ammonium chloride in the solution lowered

¹ Bosek, *J. Chem. Soc.*, 1895, 67, 515; Brauner, *loc. cit.*

² Tocco, *Gazzetta*, 1924, 54, 23.

³ Rose, *Pogg. Annalen*, 1853, 89, 131; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 13, 27; Mourlot, *Compt. rend.*, 1896, 123, 54.

⁴ Schürmann, *Annalen*, 1889, 249, 336; de Sénarmont, *loc. cit.*; Rose, *loc. cit.*

⁵ Carnot, *loc. cit.*

⁶ Rose, *Pogg. Annalen*, 1853, 89, 132, 138; Lang, *Ber.*, 1885, 18, 2716; Ditte, *Compt. rend.*, 1886, 102, 212.

⁷ Fuchs, *Compt. rend.*, 1834, 31, 578; Rose, *Pogg. Annalen*, 1853, 89, 123. See, however, Ditte, *loc. cit.*

⁸ Guinchant and Chrétien, *Compt. rend.*, 1904, 139, 51.

⁹ Vortmann, *Ber.*, 1889, 22, 2311; Vohl, *Annalen*, 1855, 96, 240; Lenssen, *Annalen*, 1860, 114, 118; Fresenius, "Anleitung zur quantitativen chemischen Analyse" (Braunschweig), 1873-1877, 6th Ed., 1, 640; Lesser, *Inaug. Dissertation*, Berlin, 1880; Orłowski, *Zeitsch. anal. Chem.*, 1883, 22, 358; Vortmann, *Monatsh.*, 1886, 7, 421; Carnot, *Compt. rend.*, 1886, 103, 258.

¹⁰ Hansen, *Zeitsch. angew. Chem.*, 1932, 45, 505, 521; Kurtenacker and Furstenau, *Zeitsch. anorg. Chem.*, 1933, 215, 257.

¹¹ Sharples, *Chem. News*, 1870, 22, 190; *Zeitsch. anal. Chem.*, 1871, 10, 343; Rose, *loc. cit.*; Duflos, *Schweigger's J.*, 1830, 62, 210; 1833, 67, 269; Finkener, *J. Soc. Chem. Ind.*, 1889, 8, 733; *Chem. Zeit.*, 1889, 13, Rep. 201; *Chem. Zentr.*, 1889, ii, 380.

the temperature at which precipitation began in each case.¹ It is probable that the precipitate of antimony sulphide obtained from hydrochloric acid solution by hydrogen sulphide is seldom pure, being contaminated with antimony oxychloride. The precipitate should be heated in an atmosphere of carbon dioxide at 250° C. in order to convert it to the black variety.²

For commercial purposes crude antimony trisulphide is usually obtained by liquation from antimony ores. The chief impurities are arsenic,³ lead,⁴ iron, copper and other metals. Purer products are obtained by melting together a mixture of finely divided refined antimony and sulphur,⁵ or by saturating a solution of antimony trioxide in dilute hydrochloric acid with hydrogen sulphide and passing carbon dioxide through the boiling liquid.⁶

Polymorphic forms of antimony trisulphide that have been investigated are the red precipitated form, the black crystalline form and the natural stibnite. The two latter appear to differ only in density.⁷ The densities of the three varieties are :

Red precipitated form	4.1205 to 4.421
Greyish-black form	4.2906
Stibnite	4.6353

Stibnite crystallises in the rhombic system⁸

$$a : b : c = 0.9926 : 1 : 1.0179$$

From X-ray examination, however, the lengths of the edges of the rhombic cell are given as⁹

$$a = 11.89 \text{ \AA.}, \quad b = 11.48 \text{ \AA.} \quad \text{and} \quad c = 3.89 \text{ \AA.}$$

giving as axial ratios

$$a : b : c = 0.992 : 1 : 0.338$$

There are four molecules of Sb_2S_3 in the unit cell.¹⁰

Transformation from the orange-red to the black variety takes place on heating at just over 200° C., with evolution of heat.¹¹ The influence of a number of substances on the transformation point, including carbon dioxide, hydrogen sulphide, ammonium chloride, antimony trichloride, metallic silver, potassium nitrate, sodium chloride, ammonium sulphate, and acids of different concentrations, has been investigated.¹² In the presence of water and various ions,¹³ raising the temperature to 75° C. hastens the change, the order of effectiveness of various ions and water

¹ Luff, *Chem. Zeit.*, 1921, 45, 229, 249, 254, 274; Prim, *ibid.*, 1917, 41, 414.

² Youtz, *J. Amer. Chem. Soc.*, 1908, 30, 375; Beckett, *Chem. News*, 1910, 102, 101.

³ Wackenroder, *Arch. Pharm.*, 1852, [2], 71, 257; Reichardt, *Arch. Pharm.*, 1857, [2], 91, 136.

⁴ Wittstein, *Repertorium Pharmacie*, 1850, [3], 5, 67; Reichardt, *loc. cit.*

⁵ von Liebig, *Magazin der Pharmacie*, 1831, 35, 120; *Annalen*, 1833, 7, 1; 1859, 31, 57.

⁶ Mitchell, *Chem. News*, 1893, 67, 291.

⁷ Zani, *Bull. Acad. roy. Belg.*, 1909, 1169.

⁸ Dana, "System of Mineralogy" (New York and London), 1899, 6th Ed., p. 36; Dana, *Amer. J. Sci.*, 1883, [3], 26, 214; Palache and Modill, *Amer. Mineral.*, 1930, 15, 365; Hofmann, *Zeitsch. Krist.*, 1933, 86, 225; Hintze, *ibid.*, 1882, 6, 410.

⁹ Gottfried, *Zeitsch. Krist.*, 1927, 65, 428; Allbright, *Phys. Review*, 1931, 37, 458.

¹⁰ Hofmann, *loc. cit.*

¹¹ Zani, *loc. cit.*; de Bacho, *Annale Chim. appl.*, 1919, 12, 143.

¹² Wilson and McCroskey, *J. Amer. Chem. Soc.*, 1921, 43, 2178.

¹³ Lehrmann, *J. Physical Chem.*, 1931, 35, 2763.

being (in diminishing order): anions, $S^{=}$, water, NO_3^- , Cl^- , $SO_4^{=}$, $C_2H_3O_2^-$; cations, H^+ , water, Na^+ , NH_4^+ . In aqueous hydrochloric acid the times taken for complete transformation in solutions of concentrations 12*N*, 7*N* and *N* were 0.5 day, 1 day and 10.5 days respectively. The effect of temperature on the time taken for the transformation (using a 20 per cent. solution of hydrogen chloride) was as follows:

Temp., °C. .	26.5°	30°	35°	40°	68.5°	75°
Time required .	44 hrs.	29 hrs.	16 hrs.	9 hrs.	62 mins.	32 mins.

In a corresponding solution of hydrogen bromide no change occurred after 20 hours at 75° C.

The hardness of stibnite on Mohs' scale is 2 to 2.5. Its density¹ and that of the prepared variety² have already been given. Its melting point is about 550° C.³ It can be distilled, the boiling point being 1090° to 1150° C.; some decomposition takes place.⁴ Antimony trisulphide begins to volatilise at 650° C.; volatilisation is rapid at 800° to 850° C. and is complete at 917° C. The electrical conductivity of single crystals is not purely electronic, electrolytic decomposition accompanying prolonged passage of current.⁵

Amorphous antimony trisulphide varies in properties according to the method of preparation. In colour it ranges from red to greyish-black. Most specimens contain water, and it has been suggested that a hydrate is formed; also that the black form is anhydrous and the red form hydrated.⁶ It has been observed, however, that the loss in weight which occurs when the red variety is heated to 100° C. is not due so much to loss of water as to secondary reactions involving absorption of oxygen and loss of sulphur dioxide.⁷ When the sulphide is precipitated from a solution free from chlorides it does not suffer any loss in weight on prolonged heating at 250° C. in a current of carbon dioxide.⁸ The densities of different specimens⁹ vary from 4.120 to 4.421. An investiga-

¹ Neumann, *Pogg. Annalen*, 1831, 23, 1; Schröder, *Jahresber.*, 1879, 54.

² Ditte, *Compt. rend.*, 1886, 102, 212; Rose, *Pogg. Annalen*, 1853, 89, 131; Karsten, *Schweigger's J.*, 1832, 65, 395; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 12, 127; Guinchant and Chrétien, *Compt. rend.*, 1906, 142, 709.

³ Pélabon, *Compt. rend.*, 1904, 138, 277; Guinchant and Chrétien, *ibid.*, 1904, 138, 1269.

⁴ Britzke and Zaetev, *Mineralnœ Svir'e*, 1931, 5, 816; Kohlmeier, *Metall und Erz*, 1932, 29, 105, 408; Shakhov and Slobodska, *Tzvet. Met.*, 1930, 1294; *Chimie et Industrie*, 1931, 25, 1126.

⁵ Frey, *Arkiv Kemi, Mineral., Geol.*, 1932, 11 A, No. 4, 1.

For other physical properties, see Pélabon, *Compt. rend.*, 1905, 140, 1389; Regnault, *Pogg. Annalen*, 1841, 53, 75; Neumann, *Jahresber.*, 1864, 50; Olie, Jun. and Kruyt, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 740; Voigt, *Zeitsch. Physik*, 1929, 57, 154; Cissarz, *Neues Jahrb. Min.*, 1931, A 64, 137; *Chem. Zentr.*, 1932, i, 512; Yamaguti, *Proc. Phys.-Math. Soc. Japan*, 1932, 14, 1.

⁶ Ditte, *loc. cit.*; Wittstein, *Zeitsch. anal. Chem.*, 1870, 9, 264; Rose, *Pogg. Annalen*, 1853, 89, 137; Fresenius, "*Anleitung zur quantitativen chemischen Analyse*" (Braunschweig), 1873-1877, 6th Ed., 2, 812; Dexter, *Amer. J. Sci.*, 1868, [2], 45, 78; Nilson, *Zeitsch. anal. Chem.*, 1877, 16, 418; Cooke, *Proc. Amer. Acad. Arts Sci.*, 1877, 12, 127; Unger, *Arch. Pharm.*, 1871, [2], 148, 11.

⁷ Zani, *loc. cit.*

⁸ Youtz, *J. Amer. Chem. Soc.*, 1908, 30, 375.

⁹ Fuchs, *Pogg. Annalen*, 1834, 31, 578; Rose, *loc. cit.*; Cooke, *loc. cit.*; Guinchant and Chrétien, *Compt. rend.*, 1904, 139, 51.

tion of the heat of formation of different specimens reveals only very slight differences.¹ The calculated heat of formation (from sulphur vapour and solid antimony)² is 86,490 gram-calories, and that from rhombic sulphur and solid antimony 38,300 gram-calories (both calculations refer to black antimony trisulphide).³

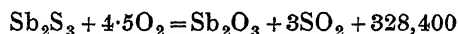
The chemical properties of all varieties of the trisulphide are similar, but the amorphous form is the most active. All varieties are decomposed when heated, metallic antimony being formed.⁴

Antimony trisulphide is reduced by hydrogen, reduction beginning at 360° C. The reaction



is reversible.⁵ From a study of the equilibrium between antimony trisulphide and hydrogen the dissociation pressures of the trisulphide have been calculated,⁶ and it is found that $\log p$ is a linear function of T , where p is the partial pressure of the sulphur vapour and T the absolute temperature.⁷ At temperatures up to the melting point, the partial pressure of hydrogen sulphide is proportional to the temperature;⁸ above the melting point the equilibrium is disturbed owing to the solubility of metallic antimony in molten antimony sulphide, the composition of the gas then depending not only on the temperature, but also on the concentration of the solution of antimony in antimony trisulphide. If antimony is present in excess, the solution is, of course, always saturated, and again the equilibrium is determined by temperature alone. Antimony trisulphide reacts with hydrogen under the influence of the silent electric discharge (15,000 volts), the products being an antimony mirror and hydrogen sulphide.⁹

Antimony trisulphide burns in oxygen with the formation of sulphur dioxide and a mixture of antimony trioxide and tetroxide.¹⁰ The heat of reaction has been calculated¹¹ and is given, in gram-calories, by the equation



The conditions of roasting antimony trisulphide have also been studied,¹² together with the conditions of oxidation to antimony trioxide and antimony tetroxide, and the dissociation of the latter. At 190° C. oxidation to antimony trioxide begins, the action becoming rapid at 340° C. and complete at 445° C. Above this temperature oxidation to antimony tetroxide takes place, and continues up to 900° C., at which temperature dissociation of the latter into antimony trioxide begins and

¹ Guinchant and Chrétien, *loc. cit.*; Berthelot, *Ann. Chim. Phys.*, 1887, [6], 10, 135; *Compt. rend.*, 1904, 139, 97.

² Britzke and Kapustinski, *Tsvet. Met.*, 1931, 1147.

³ Britzke and Kapustinski, *J. Phys. Chem.*, U.S.S.R., 1934, 5, 85.

⁴ Mourlot, *Compt. rend.*, 1896, 123, 55; *Ann. Chim. Phys.*, 1899, [7], 17, 510.

⁵ Rose, *Pogg. Annalen*, 1824, 3, 443; Schneider, *ibid.*, 1856, 98, 296; *J. prakt. Chem.*, 1880, [2], 22, 137.

⁶ Britzke and Kapustinski, *loc. cit.*; *Zeitsch. anorg. Chem.*, 1930, 194, 323.

⁷ See also Kohlmeyer, *Metall und Erz*, 1932, 29, 105, 481.

⁸ Pélabon, *Compt. rend.*, 1900, 130, 911.

⁹ Miyamoto, *J. Chem. Soc. Japan*, 1932, 53, 788.

¹⁰ Capitaine, *J. Pharm. Chim.*, 1839, [3], 25, 516; Jannasch, *Zeitsch. anorg. Chem.*, 1894, 6, 303; Haidinger, *Pogg. Annalen*, 1827, 11, 178; Eakle, *Zeitsch. Kryst.*, 1894, 24, 581; Laspeyres, *ibid.*, 1884, 9, 186.

¹¹ Britzke and Kapustinski, *Tsvet. Met.*, 1931, 1147.

¹² Shakhov and Slobodska, *ibid.*, 1930, 1294; *Chimie et Industrie*, 1931, 25, 1126.

is complete at 1130° C. By the action of ozone, antimony trisulphide is converted into antimony sulphate.¹

By prolonged digestion with water the amorphous trisulphide decomposes, yielding antimony trioxide and hydrogen sulphide.² It reacts with steam to form an oxysulphide.³ It is oxidised by hydrogen peroxide to sulphate,⁴ and even to pentoxide;⁵ ammoniacal solutions of hydrogen peroxide and sodium peroxide react to form antimonates.⁶

Antimony trisulphide reacts vigorously with fluorine in the cold, yielding the trifluoride.⁷ Chlorine reacts less vigorously with the heated sulphide, which, however, is decomposed by hydrogen chloride.⁸ The trisulphide will dissolve in aqueous hydrochloric acid, the solubility depending upon the concentration of the acid and of the hydrogen sulphide in the solution. If the pressure of hydrogen sulphide over the solution is increased, the action is reversed and antimony trisulphide is precipitated. Complete dissolution can be obtained by removal of hydrogen sulphide.⁹ Antimony trisulphide is also decomposed by bromine¹⁰ and by iodine.¹¹ (For the influence of the halogen acids upon the transformation of the amorphous into the crystalline variety, see p. 101.)

Thermal examination of a number of binary sulphide systems in which antimony trisulphide forms one component has been made. This includes the systems with bismuth trisulphide,¹² lead sulphide,¹³ tin sulphide,¹⁴ cuprous sulphide,¹⁵ silver sulphide.¹⁶ The ternary systems copper-antimony-sulphur¹⁷ and nickel-antimony-sulphur¹⁸ have been examined.

Sulphur dioxide has very little action on antimony trisulphide.¹⁹ The

¹ Mailfert, *Compt. rend.*, 1882, 94, 1186.

² Geiger and Hesse, *Annalen*, 1833, 7, 19; Vogel, *J. Pharm.*, 1822, 8, 148; de Clermont and Frommel, *Ann. Chim. Phys.*, 1879, [5], 18, 198; *Compt. rend.*, 1878, 86, 828; 1878, 87, 330; Elbers, *Chem. Zeit.*, 1888, 12, 355; Lesser, *Inaugural Dissertation, Berlin*, 1886; Lang, *Ber.*, 1885, 18, 2715; Dölter, *Monatsh.*, 1890, 11, 149.

³ Régnault, *Ann. Chim. Phys.*, 1836, [2], 62, 383.

⁴ Classen and Bauer, *Ber.*, 1883, 16, 1067; Thénard, *Ann. Chim.*, 1800, 32, 257.

⁵ Zambelli and Luzzatto, *Ann. chim. farm.*, 1886, [4], 3, 229.

⁶ Hampe, *Chem. Zeit.*, 1895, 18, 1899.

⁷ Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 262.

⁸ Tookey, *J. Chem. Soc.*, 1862, 15, 462; de Koninck and Lecrenier, *Zeitsch. anal. Chem.*, 1888, 27, 462.

⁹ Lang, *Ber.*, 1885, 18, 2714; Lang and Carson, *J. Soc. Chem. Ind.*, 1902, 21, 1018; Warren, *Chem. News*, 1892, 65, 232. For the application of this reaction in analysis, see Field, *Chem. News*, 1861, 3, 114; Lesser, *Inaugural Dissertation, Berlin*, 1886; Stromeyer, *Zeitsch. anal. Chem.*, 1870, 9, 264; Köhler, *ibid.*, 1890, 29, 192; Neher, *ibid.*, 1893, 32, 50; Loviton, *J. Pharm. Chim.*, 1888, [5], 17, 361; *Zeitsch. anal. Chem.*, 1890, 29, 345; Schleier, *Inaugural Dissertation, Erlangen*, 1892.

¹⁰ Jannasch and Remmler, *Ber.*, 1893, 26, 1422; Bartley, *American Chemist*, 1875, 5, 436.

¹¹ Schneider, *Pogg. Annalen*, 1856, 99, 470; 1860, 109, 610; 1860, 110, 150; Bolton, *Chem. News*, 1878, 38, 168.

¹² Takahashi, *Mem. Coll. Sci. Kyōtō*, 1920, 4, 47.

¹³ Jaeger and van Klooster, *Zeitsch. anorg. Chem.*, 1912, 78, 245; Iitsuka, *Mem. Coll. Sci. Kyōtō*, 1920, 4, 61.

¹⁴ Parravano and de Cesaris, *Atti R. Accad. Lincei*, 1912, [5], 21, i, 535.

¹⁵ Chikashige and Yamanchi, *Mem. Coll. Sci. Kyōtō*, 1916, 1, 341.

¹⁶ Jaeger and van Klooster, *loc. cit.*; Konno, *Mem. Coll. Sci. Kyōtō*, 1920, 4, 51.

¹⁷ Guertler and Meissner, *Metall und Erz*, 1921, 18, 410.

¹⁸ Guertler and Schack, *Metall und Erz*, 1923, 20, 162.

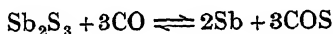
¹⁹ Berthier, *Ann. Chim. Phys.*, 1823, [2], 22, 239; Guerout, *Compt. rend.*, 1872, 75, 1276. See also Bunsen, *Annalen*, 1858, 106, 8; 1878, 192, 305; Nilson, *Zeitsch. anal. Chem.*, 1877, 16, 419; 1879, 18, 166.

trisulphide is dissolved slowly by concentrated sulphuric acid, yielding an acid antimony sulphate, sulphur dioxide and sulphur.¹ Dilute sulphuric acid assists the transformation from the amorphous variety to the crystalline. By heating with potassium sulphate, potassium antimonate is obtained.² The trisulphide reacts with both sulphuryl chloride and thionyl chloride, antimony trichloride being formed in each case.³

Antimony trisulphide is appreciably soluble in aqueous ammonia, the solubility increasing with rise of temperature. In solutions of ammonium carbonate, however, it is practically insoluble.⁴ Treatment with concentrated nitric acid yields a mixture of antimony nitrate and sulphate, and with fuming nitric acid a mixture of antimony pentoxide and sulphuric acid.⁵ Hydrogen sulphide is evolved by the action of slightly diluted nitric acid (6*N*); this action is retarded by the presence of hydrazine. In the presence of the latter a number of secondary reactions also occurs.⁶ The trisulphide is completely converted to trichloride by heating with a mixture of ammonium chloride and ammonium nitrate.⁷

A complex reaction takes place when antimony trisulphide is heated in a current of phosphine, the products being phosphorus, antimony and hydrogen sulphide.⁸

Antimony trisulphide is reduced to metallic antimony when heated with carbon, carbon disulphide also being formed;⁹ it is partially reduced by heating in a current of carbon monoxide at red heat.¹⁰ In the reaction



equilibrium moves to the right with rise of temperature.¹¹ Antimony trisulphide also reacts with carbon dioxide at a dull red heat, the products including sulphur dioxide, carbon monoxide and carbonyl sulphide.¹²

When antimony trisulphide is fused with excess of alkali, a mixture of alkali antimonite and thioantimonite is produced; but if excess of the trisulphide is used, antimony oxysulphide is obtained instead of alkali antimonite;¹³ some metallic antimony may be precipitated if the fusion is carried out at a high temperature. Amorphous antimony trisulphide is soluble in excess of an aqueous solution of potassium hydroxide, but is reprecipitated on the addition of hydrochloric acid; the crystalline form behaves similarly on warming.¹⁴ When heated with potassium

¹ Hensgen, *Rec. Trav. chim.*, 1885, 4, 401.

² Websky, *Zeitsch. anal. Chem.*, 1872, 11, 121.

³ Prinz, *Annalen*, 1884, 223, 364; Ruff, *Ber.*, 1901, 34, 1752.

⁴ Epik, *Zeitsch. anal. Chem.*, 1932, 89, 17; Garot, *J. prakt. Chem.*, 1843, 29, 83; Garnier, *J. Pharm. Chim.*, 1893, [5], 28, 97; Capitaine, *ibid.*, 1839, [3], 25, 516; *J. prakt. Chem.*, 1839, 18, 449.

⁵ Bunsen, *Annalen*, 1858, 106, 3.

⁶ Kesans, *Latv. Univ. Raksti*, 1933, 2, 311, 317.

⁷ Fresenius, *Zeitsch. anal. Chem.*, 1886, 25, 200; de Clermont, *Compt. rend.*, 1879, 88, 972.

⁸ Rose, *Pogg. Annalen*, 1830, 20, 336.

⁹ Berthier, *Ann. Chim. Phys.*, 1823, 22, 239.

¹⁰ Gobel, *J. prakt. Chem.*, 1835, 6, 388.

¹¹ Britzke and Zaetev, *Mineralnoe Svir'e*, 1931, 5, 816.

¹² de Bacht, *Monatsh.*, 1916, 37, 85.

¹³ Berzelius, *Schweigger's J.*, 1822, 34, 58; *Pogg. Annalen*, 1830, 20, 365; 1836, 37, 163.

¹⁴ See also Weppen, *Ber.*, 1875, 8, 525; Terreil, *Bull. Soc. chim.*, 1876, [2], 25, 98.

cyanide, partial reduction takes place; ¹ on heating with a mixture of potassium cyanide and sodium carbonate a mirror is obtained when the reaction is conducted in a current of hydrogen, but not when carbon dioxide is substituted for hydrogen.²

Antimony trisulphide is reduced by heating with many metals, metallic antimony being formed, which combines with excess of the metal to form antimonides.³

Sols of antimony trisulphide have been obtained by the action of hydrogen sulphide upon water saturated with antimony trioxide;⁴ or upon a dilute solution of potassium antimonyl tartrate;⁵ or by the addition of a few drops of a solution of potassium sulphide to a suspension of amorphous antimony trisulphide in water.⁶ These sols vary in colour from blood-red to yellow. They may be purified by dialysis, tartaric acid, however, being difficult to separate. Sols free from foreign matter are stable even on warming. Many acids and their salts cause precipitation of the trisulphide, the efficiency of a salt in this respect increasing with the valency of the cation. (Iron, however, appears to act exceptionally.⁷)

Two hydrates of antimony trisulphide, namely $\text{Sb}_2\text{S}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$, have been described, but their existence does not appear to have been established definitely.⁸

From an examination of the precipitates obtained by the action of hydrogen sulphide upon potassium antimonyl tartrate it has been assumed that compounds of antimony trisulphide with hydrogen sulphide may exist. The precipitates, however, are of variable composition.⁹

Compounds of antimony trisulphide with metallic sulphides have been described. These have generally been assumed to be complex *thioantimonites*, related to a number of hypothetical, and complex, thio-antimonious acids. Compounds of the types Na_3SbS_3 , $\text{Na}_2\text{Sb}_4\text{S}_7$, $\text{Na}_6\text{Sb}_4\text{S}_9$, NaSbS_2 and NaHSb_4S_7 have been described. Many of them occur naturally (see pp. 4–8). They may be prepared by fusion, or by the action of antimony trisulphide upon solutions of the metallic sulphides. Alkali thioantimonites may be prepared by the action of alkali hydroxide,

¹ Rose, *Pogg. Annalen*, 1853, 90, 204.

² Fresenius, "Anleitung zur qualitativen chemischen Analyse" (Braunschweig), 1919, p. 314.

³ For the chemical reactions of antimony trisulphide with other metallic compounds, see Ephraim, *Zeitsch. anorg. Chem.*, 1905, 44, 195; Böttger, *Jahresber.*, 1869, 1065; Verneuil, *Compt. rend.*, 1886, 103, 600; Becquerel, *Compt. rend.*, 1888, 107, 895; Zsigmondy, *Dingl. poly. J.*, 1889, 273, 29; Schürmann, *Annalen*, 1889, 249, 341; Lindner, *Zeitsch. Chem.*, 1869, 442; Bunsen, *Annalen*, 1858, 106, 4.

⁴ Capitaine, *J. Pharm.*, 1839, 25, 516; *J. prakt. Chem.*, 1839, 18, 49; Schulze, *J. prakt. Chem.*, 1880, [2], 27, 320.

⁵ Picton, *J. Chem. Soc.*, 1892, 61, 137; Schulze, *loc. cit.*

⁶ Ditte, *Compt. rend.*, 1886, 102, 169.

⁷ See also Biltz and Geibel, "Abhandlungen der Königl. Gesellschaft der Wissenschaften zu Göttingen," 1906, 141; 1904, 1; Lubavin, *J. Russ. Chem. Soc.*, 1889, 21, 397; Sabanejew, *Wied. Annalen*, 1891, 15, 755; Jablczynski and Przewdzicka-Jedrzejowska, *Bull. Soc. chim.*, 1925, [4], 37, 608; *Rocz. Chem.*, 1925, 5, 173; Ghosh and Dhar, *Kolloid Zeit.*, 1925, 36, 129; Sen, Ganguly and Dhar, *J. Physical Chem.*, 1924, 28, 313; Clemente and Hwei-Pu Tsai, *Univ. Philippines Natural Applied Science Bulletin*, 1931, 1, 319; Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, 8, 11; Jablczynski, *Kolloid Zeit.*, 1931, 54, 164.

⁸ Ditte, *Compt. rend.*, 1886, 102, 214; Dexter, *Zeitsch. anal. Chem.*, 1870, 9, 264; Wittstein, *ibid.*, 1870, 9, 267; Nilson, *ibid.*, 1877, 16, 418; Matthiew-Plessy, *Bulletin de la Société industrielle de Mulhouse*, 1855, No. 130.

⁹ Linder and Picton, *J. Chem. Soc.*, 1892, 61, 133.

carbonate or sulphide upon antimony trisulphide; or by the action of alkali sulphide upon antimony trichloride. Corresponding compounds of the heavy metals may be obtained by double decomposition.¹ Thioantimonites of alkali and alkaline earth metals (formerly known as "liver of antimony") vary in colour from yellow to reddish-brown, those containing the greater proportion of antimony trisulphide having the darker colour. Crystalline specimens can be prepared. They melt at a low temperature, and are fairly stable when gently heated out of contact with air; they decompose when heated strongly, being converted into thioantimonates. When heated in air they burn. Thioantimonites of the heavy metals are grey to black in colour, the natural products being crystalline, synthetic products amorphous. Some of them can be melted without decomposition when heated in the absence of air; but for the most part they decompose readily, forming a sublimate of antimony trisulphide. Heated in air, they are converted to oxides, with evolution of sulphur dioxide.

Only the thioantimonites of the alkali and alkaline earth metals are soluble in water. They are for the most part hygroscopic, and many are decomposed, as are also their solutions, on exposure to air. The natural thioantimonites are decomposed by the action of nitric acid and other oxidising agents, and in some cases by hydrochloric acid.² They are completely decomposed by solutions of alkali sulphides.³

The existence of antimony tetrasulphide, Sb_2S_4 , which has been described as a reddish-yellow or red powder, does not appear to have been fully established. Several methods for the preparation of this powder have been described, including the action of hydrogen sulphide upon a hydrochloric acid solution of antimony tetroxide, or potassium meta-hypoantimonate, $\text{K}_2\text{Sb}_2\text{O}_5$, or upon a solution of the complex compound $3\text{KCl} \cdot 2\text{SbCl}_4$; ⁴ and the action of carbon disulphide upon antimony pentasulphide.⁵ On heating it is converted to antimony trisulphide. It dissolves in hydrochloric acid yielding hydrogen sulphide; it also dissolves in ammonia forming a yellow solution.⁶ More recently it has been suggested that golden antimony sulphide, generally regarded as impure antimony pentasulphide, is really a mixture

¹ Berzelius, *Schweigger's J.*, 1812, 6, 144; 1818, 22, 69; 1822, 34, 58; *Pogg. Annalen*, 1830, 20, 365; 1836, 37, 163; Ditte, *Compt. rend.*, 1886, 102, 168, 212; Pouget, *ibid.*, 1898, 126, 1144; *Ann. Chim. Phys.*, 1899, 18, 524; Stanek, *Zeitsch. anorg. Chem.*, 1898, 17, 117; Unger, *Arch. Pharm.*, 1871, [2], 147, 198; 1871, [2], 148, 2; Berthelot, *Ann. Chim. Phys.*, 1887, [6], 10, 133; Duflos, *Schweigger's J.*, 1831, 62, 210; 1833, 67, 269; Rammelsberg, *Pogg. Annalen*, 1841, 52, 204; Sommerlad, *Zeitsch. anorg. Chem.*, 1897, 15, 173; 1898, 18, 420.

² Pouget, *Compt. rend.*, 1897, 124, 1445; 1898, 126, 1792; Classen, *Ber.*, 1894, 27, 2074; Hampe, *Zeitsch. anal. Chem.*, 1892, 31, 320; Jannasch, *J. prakt. Chem.*, 1889, [2], 40, 230; *Zeitsch. anal. Chem.*, 1894, 33, 214; Berthelot, *Ann. Chim. Phys.*, 1886, [6], 10, 134; Bolton, *Chem. News*, 1878, 37, 99; 38, 168; Muller, *Pogg. Annalen*, 1866, 127, 413; Marx, *Schweigger's J.*, 1830, 59, 251; Kohl, *Archiv des Apothekervereins im nördlichen Deutschland*, 1826, 17, 259; Berthier, *Ann. Chim. Phys.*, 1823, 22, 239; 1824, 25, 379.

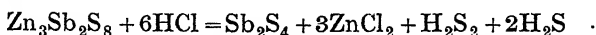
³ Dolter, *Monatsh.*, 1890, 11, 150; Terreil, *Compt. rend.*, 1870, 69, 1360. See also Pouget, *ibid.*, 1897, 124, 1445; 1899, 129, 103; Poleck, *Ber.*, 1894, 27, 1052; Serono, *Gazzetta*, 1894, 24, II, 274; Smith, *Ber.*, 1890, 23, 2276; Berglund, *Ber.*, 1884, 17, 95; Heumann, *Annalen*, 1874, 173, 33.

⁴ Bosek, *J. Chem. Soc.*, 1895, 67, 516.

⁵ Mitscherlich, *J. prakt. Chem.*, 1840, 19, 455; Wilm, *Zeitsch. anal. Chem.*, 1891, 30, 438; Brauner, *J. Chem. Soc.*, 1895, 67, 540.

⁶ Capitaine, *J. Pharm.*, 1839, 25, 516; *J. prakt. Chem.*, 1839, 18, 449. See also Websky, *Zeitsch. anal. Chem.*, 1872, 11, 124.

of antimony tetrasulphide, antimony trisulphide and free sulphur; it is further claimed that pure antimony tetrasulphide may be obtained by decomposing zinc thioantimonate with dilute hydrochloric acid, according to the equation.

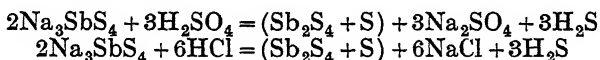


The tetrasulphide is regarded as being of the type $\text{M}_x(\text{SbS}_4)_y$, in the special case when $\text{M} = \text{Sb}$ and $x = y$.¹

Antimony Pentasulphide, Sb_2S_5 , appears to have been first described by Basil Valentine. Early writers knew it as *sulphur auratum*, while Glauber (1654) described it in his "*Pharmacopœia spagyrica*" as *Panacea Antimonialis*.²

It is doubtful if pure antimony pentasulphide has been prepared, most samples, and certainly all commercial products, containing free sulphur; possibly no higher sulphide exists than antimony tetrasulphide.³ A fairly pure product may be obtained by passing hydrogen sulphide through a solution containing antimony pentachloride (free from tervalent antimony) and 12 to 15 per cent. free hydrochloric acid.⁴ After treatment with carbon disulphide the resulting substance has a composition corresponding to Sb_2S_5 , and does not react with ammoniacal silver nitrate.

Commercial antimony pentasulphide, or "golden antimony sulphide," is as already stated always impure, and is generally supposed to be a mixture of antimony tetrasulphide and free sulphur. The usual method of preparation is by the decomposition of an alkali thioantimonate, such as Schlippe's salt, Na_3SbS_4 , by means of dilute acid:—



Sulphurous acid has also been suggested,⁵ and is recommended in preference to the stronger acids since the evolution of hydrogen sulphide by the latter is objectionable. When sulphurous acid is used, the formation of excess of free sulphur (which would contaminate the product) may be prevented by the careful addition of sodium sulphite.⁶ In order to avoid the production of brownish products the solution must be kept acid.⁷

Antimony pentasulphide is a reddish-yellow or brown powder with a faint smell and a sweetish taste. When heated it loses sulphur, darkens in colour, and at 170° C. is gradually converted into antimony

¹ Kirchhof, *Zeitsch. anorg. Chem.*, 1920, 112, 67.

² Dyson, *Pharm. J. and Pharmacist*, 1929, [4], 67, 397, 520.

³ Kirchhof, *Zeitsch. anorg. Chem.*, 1920, 112, 67; Short and Sharpe, *India-rubber J.*, 1922, 63, 379; *J. Soc. Chem. Ind.*, 1922, 41, 109 T.

⁴ Schürmann and Böhm, *Kautschuk*, 1930, 6, 70, 91, 136. See also Ullmann, "*Enzyklopädie der technischen Chemie*" (Berlin and Vienna), 1928, 2nd Ed., 1, 548.

⁵ Farbenind. (Hansen), *German Patent*, 1926, 492686.

⁶ Hansen, *Zeitsch. angew. Chem.*, 1932, 45, 505, 521.

⁷ See also Bertsch and Harmsen, *German Patent*, 1896, 94124; *Zeitsch. angew. Chem.*, 1897, 641; Souviron, *French Patent*, 1925, 605401; Hahn, *U.S. Patent*, 1928, 1671203; Stark, *U.S. Patent*, 1927, 1633754; Berzelius, *Schweigger's J.*, 1822, 34, 58; *Pogg. Annalen*, 1830, 20, 365; 1836, 37, 163; Rose, *ibid.*, 1824, 3, 441; Bosek, *J. Chem. Soc.*, 1895, 67, 515; Klenker, *J. prakt. Chem.*, 1899, [2], 59, 150, 353; Bunsen, *Annalen*, 1878, 192, 317; Wittstein, *Vierteljahrsschrift für praktische Pharmacie*, 1869, 18, 531; Classen and Bauer, *Ber.*, 1883, 16, 1067; Wilm, *Zeitsch. anal. Chem.*, 1891, 30, 444; Thiele, *Annalen*, 1891, 263, 371; Brauner, *J. Chem. Soc.*, 1895, 67, 527; Prunier, *J. Pharm. Chim.*, 1896, [6], 3, 289.

trisulphide.¹ When heated in air it is oxidised to antimony trioxide,² which volatilises. It is reduced to metal by heating in a current of hydrogen, and is decomposed by exposure to moist air, antimony trioxide being formed.³ It is only partially oxidised by treatment with ammoniacal hydrogen peroxide.⁴

The pentasulphide is partially soluble in ammonium hydroxide, forming a yellowish solution and leaving as residue a mixture of antimony trisulphide and sulphur.⁵ It is decomposed by nitric acid,⁶ and by hydrochloric acid (density 1.12) forming antimony trichloride, sulphur and hydrogen sulphide;⁷ treatment with sulphuryl chloride converts it into antimony pentachloride.⁸

From most commercial samples of antimony pentasulphide sulphur can be removed by treatment with carbon disulphide, or other solvents of sulphur, the proportion removed depending upon the method of preparation of the pentasulphide.⁹

Alkali hydroxides and carbonates react with antimony pentasulphide with formation of a mixture of alkali antimonates and thioantimonates, the former being precipitated. From the solutions obtained on filtering, antimony pentasulphide is reprecipitated by the addition of acids; while from solutions in alkali carbonate the precipitate consists of antimony trisulphide. Barium and strontium hydroxides behave in a somewhat similar manner.¹⁰ Fusion with potassium cyanide causes partial reduction, some potassium thioantimonite being formed.¹¹

Commercial antimony pentasulphide is a mixture of variable composition depending upon the method of manufacture. It is employed extensively in the rubber industry, and many methods of assay have been proposed.¹²

Thioantimonates.—Compounds of antimony pentasulphide are known to occur naturally; they have also been prepared in a variety of ways. They may be regarded as normal thioantimonates, or salts of an unknown acid, thioantimonic acid, H_3SbS_4 . Salts of the heavy metals are best prepared from those of the alkali metals by double decomposition. The most important of these salts is **sodium thioantimonate**, Na_3SbS_4 , known also as *Schlippe's salt*. It is prepared by

¹ Rose, *Pogg. Annalen*, 1853, 89, 141; Heffter, *ibid.*, 1852, 86, 421; Paul, *Zeitsch. anal. Chem.*, 1892, 31, 533.

² Classen and Bauer, *Ber.*, 1883, 16, 1071; Unger, *Arch. Pharm.*, 1871, [2], 147, 196.

³ Otto, *Annalen*, 1838, 26, 88; Jahn, *Archiv des Apothekervereins im nördlichen Deutschland*, 1828, 22, 43.

⁴ Classen and Bauer, *Ber.*, 1883, 16, 1067.

⁵ Geiger, *Magazin der Pharmacie*, 1830, 29, 241.

⁶ Pagenstecher, *Trommsdorff's Neues Journal der Pharmacie*, 1820, 3, 1, 391; Wilm, *Zeitsch. anal. Chem.*, 1891, 30, 444.

⁷ Scherer, *Zeitsch. anal. Chem.*, 1864, 3, 206. See also Classen and Bauer, *loc. cit.*; Bunsen, *loc. cit.*; Wittstein, *loc. cit.*

⁸ Ruff, *Ber.*, 1901, 34, 1752.

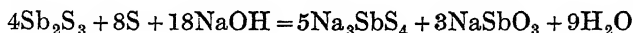
⁹ Mitscherlich, *J. prakt. Chem.*, 1840, 19, 455; Wilm, *loc. cit.*; Bosek, *loc. cit.*; Rammelsberg, *loc. cit.*; Classen, *loc. cit.*; Schurmann and Bohm, *loc. cit.*; Unger, *loc. cit.*; Klenker, *loc. cit.*

¹⁰ Mitscherlich, *loc. cit.*; Rammelsberg, *loc. cit.*; Feit and Kubierschky, *Ber.*, 1888, 21, 1660.

¹¹ Rose, *Pogg. Annalen*, 1853, 90, 207.

¹² Hook, *Kautschuk*, 1925, 1, 11; Chiappero, *Giorn. Chim. Ind. Appl.*, 1926, 8, 1020; Luff and Porritt, *J. Soc. Chem. Ind.*, 1921, 40, 275; Kirchhof, *Zeitsch. anorg. Chem.*, 1920, 114, 266; van Rossem and Dekker, *India-rubber J.*, 1920, 60, 905; Hutin, *Ann. Chim. anal.*, 1916, 21, 3, 32; Lehmann and Berdan, *Chem. Zentr.*, 1914, i, 1699; Alcock, *J. Pharm.*, 1913, 91, 213; Jacobssohn, *Chem. Zeit.*, 1908, 32, 984; *Chem. Zentr.*, 1908, i, 763; *Gummi Zeit.*, 1908, 22, 368; 1909, 23, 1046.

the gradual addition of a mixture of antimony trisulphide and sulphur to a boiling solution of sodium hydroxide,¹ according to the equation



The sodium antimonate formed at the same time is almost completely precipitated. This reaction may be employed for the preparation of other metallic thioantimonates since carbonates or sulphides of the alkali metals, or hydroxides, carbonates or sulphides of the alkaline earth metals may be used in place of sodium hydroxide.²

Thioantimonates may also be prepared by the fusion of antimony pentasulphide (or a mixture of antimony trisulphide and sulphur) with the sulphide or carbonate of an alkali metal,³ or with sodium thiosulphate.⁴ They are also obtained by the action of hydrogen sulphide upon solutions of alkali ortho-antimonates.⁵

Thioantimonates of the alkali or alkaline earth metals are either colourless or slightly yellowish; those of the heavier metals are darker in colour. Salts of the alkali and alkaline earth metals can be heated to red heat, in the absence of air, without decomposition; but in air they decompose gradually. They are soluble in water, but insoluble in alcohol; the aqueous solutions decompose on standing, and also on the addition of acids, or of carbon dioxide. Some solid thioantimonates of the heavier metals are decomposed by the action of mineral acids, with formation of antimony pentasulphide.⁶

When a solution of a thioantimonate of an alkali metal is boiled with powdered sulphur, alkali thioantimonite is obtained.⁷

Some metallic sulphides, among them being the sulphides of copper, cadmium, mercury and iron, are slightly soluble in solutions of alkali thioantimonates.⁸

A number of hydrated forms of thioantimonates of alkali metals has been prepared and described.⁹

Thermal analysis of the system antimony trioxide-antimony trisulphide (fig. 4) indicates the presence of an oxysulphide of antimony, Sb_4OS_5 , which decomposes at 522°C . This compound has also been obtained by the action of dry hydrogen sulphide upon antimony pentoxide.¹⁰ The mineral *kermesite*, $2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$ or $\text{Sb}_6\text{O}_3\text{S}_6$, corresponds

¹ Sartorius, *Chem. Zentr.*, 1908, i, 2130; *Apoth. Zeit.*, 1908, 23, 342.

² Mitscherlich, *loc. cit.*; *Pogg. Annalen*, 1840, 49, 413; Rammelsberg, *Pogg. Annalen*, 1841, 52, 206; Feit and Kubierschky, *loc. cit.*; Stanek, *Zeitsch. anorg. Chem.*, 1898, 17, 122; Duflos, *Archiv des Apothekervereins im nördlichen Deutschland*, 1829, 31, 94; Buchholz, *ibid.*, 1830, 33, 1; Prunier, *J. Pharm. Chim.*, 1896, [6], 3, 289; Pouget, *Compt. rend.*, 1898, 126, 1144; Marbach, *Pogg. Annalen*, 1856, 99, 460; Soret, *Arch. Sci. phys. nat.*, 1886, [3], 16, 468; von Liebig, *Annalen*, 1833, 7, 13; Raschig, *Ber.*, 1885, 18, 2745; Pavel, *Ber.*, 1882, 15, 2603; Classen, *Ber.*, 1886, 19, 323; Vortmann, *Ber.*, 1891, 24, 2762; Palm, *Zeitsch. anal. Chem.*, 1883, 22, 224.

³ Schlippe, *Schweigger's J.*, 1821, 33, 320.

⁴ Donath, *Zeitsch. anal. Chem.*, 1880, 19, 23. See also Becker, *Zeitsch. anal. Chem.*, 1878, 17, 185.

⁵ Rammelsberg, *Pogg. Annalen*, 1841, 52, 196, 235; Geiger, *Mag. Pharm.*, 1830, 29, 236; Brinkmann, *Inaugural Dissertation*, Erlangen, 1891; Pouget, *Ann. Chim. Phys.*, 1899, [7], 18, 542; Wackenroder, *Arch. Pharm.*, 1852, [2], 72, 257.

⁶ Wilson, *Canadian Patent*, 1924, 252563.

⁷ Duflos, *Archiv des Apothekervereins im nördlichen Deutschland*, 1830, 31, 94; 1831, 36, 278.

⁸ Storch, *Ber.*, 1883, 16, 2015. For the action of sodium thioantimonate on other metallic salt solutions, see Langhans, *Zeitsch. anal. Chem.*, 1921, 60, 91.

⁹ Donk, *Chem. Weekblad*, 1908, 5, 529; 1908, 5, 629.

¹⁰ Quercigh, *Atti R. Accad. Lincei*, 1912, [5], 21, i, 415; Schumann, *Annalen*, 1877, 187, 312.

in composition to the eutectic of antimony trioxide and the above-mentioned oxysulphide.¹ This substance is also stated to be formed by heating antimony trisulphide to a red heat in an atmosphere of steam,² by the action of dry hydrogen sulphide upon antimony trioxide, and by boiling antimony thiodiodide, SbSI , with zinc oxide and water.³ The natural mineral is a cherry-red or bright red, brilliant,

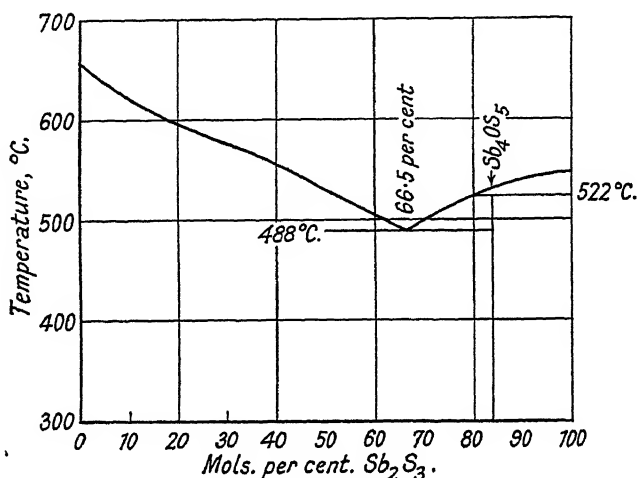


FIG. 4.—Freezing Point Curve of the System Sb_2O_3 - Sb_2S_3 .

crystalline substance belonging to the monoclinic system,⁴ having pseudo-rhombic symmetry:

$$a : b : c = 8.9650 : 1 : 0.8585; \quad \beta = 90^\circ 0'$$

Its hardness on Mohs' scale is 1.0 to 1.5, its density 4.5 to 4.6. It melts easily when heated in the blowpipe flame. It is decomposed when heated in a current of hydrogen;⁵ it is soluble in hydrochloric acid, and in a solution of potassium hydroxide, but is insoluble in a dilute solution of tartaric acid.⁶

Antimonyl Thioantimonate, $(\text{SbO})_3\text{SbS}_4$, is obtained by the action of sodium thioantimonate on potassium antimonyl tartrate.⁷

If the fused oxysulphides of antimony are cooled quickly, they are converted into glass-like substances, known sometimes as "antimony glass."

Many of the substances that have been described as oxysulphides of antimony are most probably mixtures.⁸ Some of these, known as *kermes mineral*, were formerly used medicinally. They were very

¹ Quercigh, *loc. cit.*

² Regnault, *Ann. Chim. Phys.*, 1836, 62, 383.

³ Schneider, *Pogg. Annalen*, 1860, 110, 151.

⁴ Pjanitski, *Zeitsch. Kryst. Min.*, 1891, 20, 422.

⁵ Rose, *Pogg. Annalen*, 1824, 3, 482; 1853, 89, 318.

⁶ Baubigny, *Compt. rend.*, 1894, 119, 737.

⁷ Rammelsberg, *Pogg. Annalen*, 1841, 52, 236.

⁸ Faktor, *Pharm. Post*, 1900, 33, 233; Proust, *Gilbert's Annalen*, 1807, 25, 186; Berzelius, *Schweigger's J.*, 1822, 34, 58; *Pogg. Annalen*, 1830, 20, 365; 1836, 37, 163; Werner, *J. prakt. Chem.*, 1837, 12, 53; Soubeiran, *J. Pharm.*, 1824, 10, 528; "Minière et Fonderie d'Antimonio," *German Patent*, 1905, 160110.

variable in composition. Many methods of preparation were employed.¹ A somewhat similar preparation was given in the British Pharmacopœia, under the name of *Antimonium Sulphuratum*, but has been omitted since 1932.

Allied to these oxysulphides is a potassium compound, $K_2HSbO_2S_2 \cdot 2H_2O$ (the only metallic compound of this nature that has been described), which may be obtained in the form of yellowish, needle-like crystals by the action of a moderately concentrated solution of potassium hydroxide upon antimony pentasulphide,² or upon a mixture of antimony trisulphide and sulphur.³

The existence of **sulphite of antimony** is doubtful.⁴

Normal Antimony Sulphate, $Sb_2(SO_4)_3$, may be obtained by crystallisation from a hot solution of antimony trioxide in concentrated sulphuric acid,⁵ or by the action of concentrated sulphuric acid upon antimony trisulphide or antimony sulphide ore.⁶ It crystallises in thin, four-sided prisms, density 3.6246. It is stable in dry air, but deliquesces in moist air. It is decomposed by water, forming a variety of basic compounds. It absorbs dry hydrogen chloride, and may perhaps form a complex chlorosulphate.⁷ It forms double salts, of the general formula $SbM'(SO_4)_2$, with the sulphates of the alkali metals, the alkaline earth metals and silver.⁸

Many **basic sulphates** of antimony have been described, among them being the compounds $7Sb_2O_3 \cdot SO_3$; $7Sb_2O_3 \cdot 2SO_3$; $2Sb_2O_3 \cdot SO_3$;

¹ See Polacci, *Bolletino chimico farmaceutico Mailand*, 1906, 45, 401; Bougault, *J. Pharm. Chim.*, 1903, 6, 18, 509, 547; *Compt. rend.*, 1903, 137, 497; Long, *J. Amer. Chem. Soc.*, 1896, 18, 342; Baubigny, *Compt. rend.*, 1894, 119, 687; Carnot, *ibid.*, 1886, 103, 258; *Zeitsch. anal. Chem.*, 1888, 27, 651; Teclu, *Dingl. poly. J.*, 1880, 236, 336; Weppen, *Ber.*, 1875, 8, 523; Terrell, *Compt. rend.*, 1873, 77, 1500; *Bull. Soc. chim.*, 1876, [2], 25, 98; Nilson, *Zeitsch. anal. Chem.*, 1877, 16, 424; Unger, *Arch. Pharm.*, 1871, [2], 145, 15; Akermann, *Öfvers. K. Vet. Akad. Forh.*, 1861, 235; *J. prakt. Chem.*, 1862, 86, 57; Méhu, *J. Pharm. Chim.*, 1868, [4], 8, 99; Wagner, *Wagner's Jahresber.*, 1858, 235; 1862, 331; Rieker, *Neues Jahrb. Pharm.*, 1856, 6, 260; Bottger, *J. prakt. Chem.*, 1857, 70, 437; Pettenkofer and Unger, *Dingl. poly. J.*, 1849, 113, 215; Himly, *Annalen*, 1842, 43, 150; Strohl, *J. Pharm. Chim.*, 1849, [3], 16, 11; Soubeiran, *J. Pharm.*, 1841, 27, 294; Kosmann, *J. Pharm. Chim.*, 1850, [3], 18, 321; Buchholz, *Berlinisches Jahrbuch der Pharmacie*, 1839, 29, 1, 26; Rose, *Pogg. Annalen*, 1829, 17, 324; 1833, 28, 481; 1839, 47, 323; Brandes, *Archiv des Apothekervereins im nördlichen Deutschland*, 1831, 37, 257; *Schweigger's J.*, 1831, 62, 209; Buchner, *Repertorium für die Pharmacie*, 1822, 13, 169, 203; *J. Pharm. Chim.*, 1830, [2], 16, 51; Duflos, *Archiv des Apothekervereins im nördlichen Deutschland*, 1829, 31, 94; 1831, 36, 278; *Schweigger's J.*, 1831, 62, 210; 1833, 67, 269; *Archiv für die gesamte Naturlehre*, 1830, 19, 61, 289; Gay-Lussac, *Ann. Chim. Phys.*, 1829, 42, 87; *Schweigger's J.*, 1829, 57, 252; *Pogg. Annalen*, 1829, 17, 320; Geiger, *Repertorium für die Pharmacie*, 1829, 9, 274; von Liebig, *Magazin der Pharmacie*, 1831, 35, 120; *Annalen*, 1833, 7, 1; 1839, 31, 57; Hennsmann, *Taschenbuch für Scheidekünstler und Apotheker*, 1822, 184; Henry, *J. Pharm.*, 1828, 14, 145; Pagenstecher, *Repertorium für die Pharmacie*, 1822, 14, 194, 545; Phillips, *Annals of Philosophy*, 1825, 25, 378; Vogel, *Schweigger's J.*, 1822, 33, 291; Thomson, *Schweigger's J.*, 1815, 17, 396; *Ann. Chim.*, 1815, 93, 138; Robiquet, *Ann. Chim.*, 1812, 81, 317; Schrader, *Gehlen's allg. J. Chem.*, 1807, 3, 159; Cluzel, *Ann. Chim.*, 1807, 63, 155; Thénard, *Ann. Chim.*, 1800, 32, 257; Foucroy, *Crell's Annalen*, 1778, 1, 423; Geoffroy, *Mém. Paris Acad.*, 1734, 593; 1735, 94.

² Rammelsberg, *Pogg. Annalen*, 1841, 52, 199; Schiff, *Annalen*, 1860, 114, 202; McCay, *Amer. Chem. J.*, 1896, 17, 770.

³ Weinland and Gutmann, *Zeitsch. anorg. Chem.*, 1898, 17, 414.

⁴ Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 241.

⁵ Dexter, *J. prakt. Chem.*, 1869, 106, 134; Schultz-Sellack, *Ber.*, 1871, 4, 13; Hensgen, *Rec. Trav. chim.*, 1884, 4, 101; Adie, *J. Chem. Soc.*, 1890, 57, 540.

⁶ Hensgen, *loc. cit.*; Metz, *Zeitsch. anorg. Chem.*, 1906, 48, 146; *German Patent*, 1904, 161776.

⁷ Hensgen, *loc. cit.*

⁸ Gutmann, *Arch. Pharm.*, 1898, 236, 477; 1908, 246, 187; Metz, *loc. cit.*; Kuhl, *Zeitsch. anorg. Chem.*, 1907, 54, 256.

$(\text{SbO})_2\text{SO}_4$; $3\text{Sb}_2\text{O}_3 \cdot 5\text{SO}_3$; $\text{Sb}_2\text{O}_3 \cdot 2\text{SO}_3$. They are obtained by the decomposition of normal antimony sulphate by water.¹ Basic sulphates have also been obtained by fusing either antimony or antimony trisulphide with potassium hydrogen sulphate.²

By the action of fuming sulphuric acid on antimony trioxide, an acid sulphate, $\text{Sb}_2\text{O}_3 \cdot 4\text{SO}_3$, has been obtained in the form of small, brilliant, granular crystals, readily decomposed by water.³

By adding a hydrochloric acid solution of antimony trioxide to one containing a mixture of sodium thiosulphate and the chloride of an alkali or alkaline earth metal, several metallic antimony thiosulphates, or stibiothiosulphates, have been obtained.⁴ The mixture is maintained at a temperature of about 3°C . These salts, with the exception of those of sodium, calcium and strontium, may be crystallised out by the addition of alcohol.

Potassium Stibiothiosulphate, $\text{K}_3\text{Sb}(\text{S}_2\text{O}_3)_3$, forms silk-like, needle-shaped crystals resembling asbestos. It is very soluble in water, but decomposes on boiling, with formation of the orange-red oxysulphide $\text{Sb}_6\text{O}_3\text{S}_6$. The rubidium and barium salts have also been obtained. The salts of sodium, calcium and strontium exist only in solution. The potassium salt appears to have the constitution represented by the formula $\text{Sb}[\text{S} \cdot \text{SO}_2 \cdot \text{OK}]_3$.

By the hydrolysis of these alkali stibiothiosulphates fairly stable sols of antimony pentasulphide may be obtained.⁵

ANTIMONY AND SELENIUM.

Several compounds of antimony and selenium have been reported, but it is probable that the only true compound is **antimony triselenide**, Sb_2Se_3 . Thermal analysis,⁶ supported by thermoelectric and microscopical examination, suggests that the so-called compound Sb_2Se_7 is a mixture of antimony triselenide with selenium, and that the existence of the compounds Sb_4Se_5 and Sb_3Se_4 is doubtful. Some evidence in favour of the existence of the compound SbSe has been adduced from microscopic investigation and investigations of electromotive behaviour.⁷

Antimony triselenide is obtained by the action of a saturated solution of hydrogen selenide upon a solution of an antimony salt.⁸ It is a brown powder, melting at 572°C . and soluble in hot alkali solutions. It forms compounds with other metallic selenides.⁹

Antimony pentaselenide is said to be formed by the action of hot hydrochloric acid upon a solution of sodium selenoantimonate, Na_3SbSe_4 . The pentaselenide has not been obtained, however, by precipitation with hydrogen selenide.¹⁰

¹ Metzl, *loc. cit.*; Adie, *loc. cit.*; Dexter, *loc. cit.*; Péligot, *Ann. Chim. Phys.*, 1847, [3], 20, 283.

² Websky, *Zeitsch. anal. Chem.*, 1872, 11, 124.

³ Schultz-Sellack, *Ber.*, 1871, 4, 112.

⁴ von Szilágyi, *Zeitsch. anorg. Chem.*, 1920, 113, 69.

⁵ von Hahn, *Kolloid Zeit.*, 1922, 31, 200.

⁶ Parravano, *Gazzetta*, 1913, 43, i, 210; Pélabon, *J. Chim. Phys.*, 1904, 2, 321; *Compt. rend.*, 1906, 142, 207; 1911, 153, 343; 1914, 158, 1669; *Ann. Chim.*, 1920, [9], 13, 121; Hofacker, *Annalen*, 1858, 107, 6; Chrétien, *Compt. rend.*, 1906, 142, 1339, 1412; Chikashige and Fujita, *Mem. Coll. Sci. Kyōtō*, 1917, 2, 233.

⁷ Kremann and Wittek, *Zeitsch. Metallkunde*, 1921, 13, 90.

⁸ Moser and Atynski, *Monatsh.*, 1925, 45, 235; Uelsmann, *Annalen*, 1860, 116, 124.

⁹ Pélabon, *Compt. rend.*, 1908, 146, 975. See also Padoa, *Gazzetta*, 1927, 57, 399.

¹⁰ Hofacker, *loc. cit.*; Moser and Atynski, *loc. cit.*

Two **antimony selenites**, $\text{Sb}_2\text{Se}_2\text{O}_7$ and $\text{Sb}_2\text{Se}_4\text{O}_{11}$, have been described; both were obtained by the action of selenium dioxide upon antimony trioxide.¹

Antimony Selenate, $\text{Sb}_2(\text{SeO}_4)_3$, is obtained as small, white, crystalline prisms by dissolving antimony in hot selenic acid. It is not decomposed by water, nor will it dissolve in water; it is soluble in hot selenic acid, but only slightly soluble in other acids.²

Two compounds of antimony, sulphur and selenium, $\text{Sb}_2\text{S}_2\text{Se}$ and $\text{Sb}_2\text{S}_3\text{Se}_2$, have also been described.³

Complex **selenoantimonites** and **selenoantimonates** (corresponding to the thioantimonites and thioantimonates) of sodium, potassium, and possibly of manganese, have been prepared.⁴ The selenoantimonites, $\text{Na}_3\text{SbSe}_3 \cdot 9\text{H}_2\text{O}$, $\text{K}_3\text{SbSe}_3 \cdot 9\text{H}_2\text{O}$, $\text{Na}_2\text{Sb}_4\text{Se}_7 \cdot 3\text{H}_2\text{O}$, are obtained by the action of antimony triselenide upon the corresponding alkali selenide. Sodium selenoantimonate, $\text{Na}_3\text{SbSe}_4 \cdot 9\text{H}_2\text{O}$, is obtained by fusing together antimony triselenide, selenium, sodium carbonate and carbon, extracting the melt with water and treating the solution so obtained with more selenium. Transparent, orange-yellow crystals, isomorphous with those of sodium thioantimonate, are obtained.

Still more complex compounds of sodium and potassium with antimony, sulphur and selenium have been described.⁵

ANTIMONY AND TELLURIUM.

Examination of the system antimony-tellurium indicates the existence of **antimony tritelluride**, Sb_2Te_3 , which can be melted without decomposition.⁶ Antimony tritelluride has also been prepared from solutions of antimony salts by precipitation with hydrogen telluride.⁷

ANTIMONY AND NITROGEN.

It is doubtful if direct combination occurs between antimony and nitrogen, although an unstable powder is formed when antimony is heated at a dull red heat in a current of nitrogen.⁸ **Antimony nitride** is said to be formed by the action of antimony trichloride on liquid ammonia.⁹ It is described as an orange substance, extremely sensitive to moisture; it is decomposed into the elements on heating to 500°C .

A **basic nitrate** of antimony, possibly $2\text{Sb}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$, is obtained, mixed with the oxides of antimony, by the action of nitric acid upon antimony, the formation of the nitrate being favoured by using cold acid as dilute as possible.¹⁰ The presence of nitrous acid accelerates the

¹ Nilson, *Bull. Soc. chim.*, 1875, [2], 23, 499.

² Cameron and Macallan, *Proc. Roy. Soc.*, 1889, 46, 33.

³ von Gerichten, *Ber.*, 1874, 7, 30; Hofacker, *loc. cit.*

⁴ Pouget, *Ann. Chim. Phys.*, 1899, [7], 18, 559; Hofacker, *Annalen*, 1858, 107, 6.

⁵ Pouget, *loc. cit.*; Hofacker, *loc. cit.*

⁶ Endo, *Sci. Rep. Tohoku Imp. Univ.*, 1927, 16, 201; Kimata, *Mem. Coll. Sci. Kyōtō*, 1915, 1, 115; Padoa, *Gazzetta*, 1927, 57, 399.

⁷ Brukl, *Monatsh.*, 1924, 45, 471.

⁸ Hérard, *Compt. rend.*, 1888, 107, 420.

⁹ Schwarz and Jeanmaire, *Ber.*, 1932, 65 B, 1662.

¹⁰ Buchholz, *Taschenbuch für Scheidekünstler und Apotheker*, 1806, 89; Péligot, *Ann. Chim. Phys.*, 1847, [3], 20, 283; *Annalen*, 1847, 64, 281; Rose, *Pogg. Annalen*, 1841, 53, 161; Lefort, *J. Pharm. Chim.*, 1855, [3], 28, 93.

action.¹ A somewhat similar compound is obtained by the reduction of a solution of silver nitrate with metallic antimony.²

It is stated that **normal antimony nitrate**, $\text{Sb}(\text{NO}_3)_3$, may be obtained by the action of silver nitrate upon a solution of antimony trichloride in acetone.³ The normal nitrate, however, does not appear to have been isolated.

A compound of quinquivalent antimony, $2\text{Sb}_2\text{O}_5 \cdot \text{N}_2\text{O}_5$, has been obtained by the action of nitrogen tetroxide upon a solution of antimony tribromide in chloroform, or of antimony triiodide in ether. It is a white, crystalline substance, not decomposed by water.⁴

ANTIMONY AND PHOSPHORUS.

Antimony Phosphide, SbP , has been obtained by the fusion of antimony with metaphosphoric acid⁵ or phosphorus.⁶ The substance obtained by the action of phosphorus upon a solution of antimony tribromide in carbon disulphide may perhaps be antimony phosphide.⁷

Antimonyl Dihydrogen Phosphite, $(\text{SbO})\text{H}_2\text{PO}_3$, has been obtained by the action of phosphorous acid upon antimony trioxide,⁸ and also by the action of potassium antimonyl tartrate upon an ammoniacal solution of phosphorus trichloride.⁹ It is a white powder, which, in solution in dilute hydrochloric acid, is capable of acting as a reducing agent.

Antimony Phosphate is said to be obtained by heating together either antimony or antimony trichloride and crystalline phosphoric acid; the product may be purified by treatment with acid ammonium phosphate. A dihydrate has been described, which is slightly soluble both in water and alcohol, and which is not hydrolysed when warmed with water.¹⁰

Antimony Pyrophosphate, $2\text{Sb}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$, is obtained by dissolving antimony trioxide in orthophosphoric acid;¹¹ and by boiling the trioxide with a solution of sodium pyrophosphate.¹² By hydrolysis two other substances are obtained, $4\text{Sb}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ and $2\text{Sb}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$.

Antimony Thiophosphate, SbPS_4 , is obtained as a residue, after the evolution of antimony thiochloride and phosphorus pentachloride, on heating together antimony trichloride (or antimony trisulphide) and phosphorus pentasulphide.¹³ It is a yellow powder which has an odour of hydrogen sulphide. It is decomposed by heating. It is insoluble in water, dilute hydrochloric and sulphuric acids and various organic solvents, but it is decomposed by treatment with concentrated sulphuric acid, alkalis or even ammonium hydroxide.

¹ Millon, *Ann. Chim. Phys.*, 1842, [3], 6, 101.

² Senderens, *Bull. Soc. chim.*, 1896, [3], 15, 218.

³ Naumann, *Ber.*, 1904, 37, 4333.

⁴ Thomas, *Compt. rend.*, 1895, 120, 1116.

⁵ Pelletier, *Ann. Chim.*, 1792, [1], 13, 132.

⁶ Landgrebe, *Schweigger's J.*, 1828, 53, 469.

⁷ Ramsay and MacIvor, *Ber.*, 1873, 6, 1362; see, however, Ragg, *Oesterr. Chem. Zeit.*, 1898, 1, 94.

⁸ Grutzner, *Arch. Pharm.*, 1897, 235, 694.

⁹ Rose, *Pogg. Annalen*, 1826, 9, 45.

¹⁰ Horsch, *Praktika Akad. Athenon*, 1928, 2, 517; *Chem. Zentr.*, 1928, II, 2632.

¹¹ Brandes, *Schweigger's J.*, 1831, 62, 201.

¹² Schwarzenberg, *Annalen*, 1848, 65, 2. See also Brand, *Zeitsch. anal. Chem.*, 1889, 28, 599.

¹³ Glatzel, *Ber.*, 1891, 24, 3886; *Zeitsch. anorg. Chem.*, 1893, 4, 219.

ANTIMONY AND ARSENIC.

A compound of antimony and arsenic, Sb_2As , has been described,¹ but a more recent study of the system antimony-arsenic has failed to confirm its existence.² Arsenic is frequently associated with native antimony, as in the mineral *allemontite*.³

DETECTION AND ESTIMATION OF ANTIMONY.

Dry Reactions.—Antimony compounds, when heated on charcoal in the blowpipe flame, are reduced to metal (particularly if previously mixed with fusion mixture), but the metal volatilises and burns to antimony trioxide. By depositing the oxide on a glazed porcelain surface, adding a spot of silver nitrate, and blowing a current of gaseous ammonia on to the silver nitrate a black stain is obtained. Alternatively, if the white incrustation which remains on the charcoal is moistened with ammonium sulphide solution, a deep orange stain is produced.

Wet Reactions.—When a current of hydrogen sulphide is passed through a solution containing antimony ions, an orange-coloured precipitate of antimony sulphide is obtained, the composition of which varies according to the state of oxidation of the antimony. This precipitate is more soluble than the corresponding arsenic sulphide, but less so than tin sulphide. It is soluble in alkalis and alkali sulphides (including ammonium polysulphide), and reprecipitated from solution by the addition of acid. Arsenic and tin sulphides behave similarly, but antimony may be separated from these elements and identified by one of the following methods:—

(a) Marsh's test (see p. 116) is applied, and the evolved gases passed into a neutral solution of silver nitrate. The precipitate is filtered off, washed, and treated with concentrated hydrochloric acid to dissolve any silver antimonide formed. Antimony can then be identified in this solution by dilution and treatment with hydrogen sulphide.

(b) Antimony and tin sulphides are soluble in concentrated hydrochloric acid, but arsenic sulphide is not appreciably so. If a piece of platinum foil and a little zinc are placed in this solution the presence of antimony is indicated by the formation of a black stain on the platinum, which does not disappear on removal of the zinc.

(c) Arsenic sulphide may be separated as in (b) by treatment with concentrated hydrochloric acid; antimony and tin are detected in the solution by making use of the different solubilities of their sulphides in the acid.⁴

(d) Arsenic and antimony may be detected in an acid solution containing an excess of tin by the addition of a little stannous chloride, followed by sodium bisulphite or sulphurous acid a drop at a time. The hydrogen sulphide thus liberated first precipitates arsenic trisulphide,

¹ Descamps, *Compt. rend.*, 1878, 86, 1066.

² Parravano and de Cesaris, *Internat. Zeitsch. Metallographie*, 1912, 2, 70.

³ Rammelsberg, *Pogg. Annalen*, 1844, 62, 137; Genth, *Amer. J. Sci.*, 1862, [2], 33, 190; Bizarri, *Gazzetta*, 1886, 15, 349.

⁴ Treadwell and Hall, *"Analytical Chemistry"* (New York), 5th Ed., 1921, i, 293.

and afterwards antimony trisulphide. Under these conditions no tin sulphide is precipitated.¹

An important test for antimony is *Marsh's test*, which is carried out in a manner similar to that employed for arsenic (see this Series, Vol. VI, Part IV). Stibine, which is produced in this test, is decomposed at a lower temperature than arsine, and the antimony mirror is usually formed in front of the constriction in the heated tube; this antimony mirror is not readily soluble in bleaching powder solution. (It is important that the bleaching powder solution should be freshly prepared, as old solutions always contain some chlorite, in which the antimony deposit is soluble.)² The deposits produced by arsenic and antimony in this test may be identified individually by passing a current of hydrogen sulphide through the heated tube in the reverse direction to that taken by the gases evolved from the generating flask; a yellow deposit indicates arsenic, while an orange-red deposit indicates antimony. Further confirmation may be obtained by passing a current of dry hydrogen chloride through the tube; the antimony sulphide is removed while the arsenic sulphide remains. Marsh's test for antimony is sensitive to 0.0002 mg.³

Antimony compounds are readily hydrolysed, yielding, with cold water, insoluble basic salts. If boiling water is used, hydrolysis sometimes proceeds a further stage with the formation of antimonious acid or hydrated antimony oxides. The insoluble residues arc, in general, redissolved on acidifying.

The more difficultly soluble antimony salts may be dissolved in liquids containing tartaric acid or tartrates, the resulting solutions being stable only when neutral or alkaline; on acidifying, insoluble hydroxides or hydrated oxides are produced.

Antimonious compounds may be distinguished from antimonious compounds by the action of hydriodic acid, or potassium iodide in acid solution; iodine is liberated by antimonious compounds but not by antimonious compounds.⁴

Gravimetric Methods.—The method most usually adopted for the estimation of antimony is by precipitation of the trisulphide.⁵ The sulphide, which is precipitated from a cold, acid solution (the solution being raised to boiling towards the end of the precipitation), is thoroughly washed, dried and converted to black crystalline antimony trisulphide (by heating in a current of carbon dioxide), in which form it is weighed.⁶ The black, crystalline product may be produced direct if the precipitation is carried out in a hot solution rendered strongly acid with hydrochloric acid.⁷

Antimony may also be estimated as tetroxide⁸ by precipitating first

¹ Donath, *Chem. Zeit.*, 1932, 56, 483.

² Vaubel and Knocke, *Chem. Zeit.*, 1916, 40, 209.

³ Scheuchter, *Monatsh.*, 1921, 42, 411. Also Sanger and Gibson, *J. Soc. Chem. Ind.*, 1907, 26, 585.

⁴ See also Duquénnois, *Compt. rend.*, 1933, 197, 339; Caille and Viel, *ibid.*, 1923, 176, 1156.

⁵ Henz, *Zeitsch. anorg. Chem.*, 1903, 37, 18.

⁶ Paul, *Zeitsch. anal. Chem.*, 1892, 31, 540.

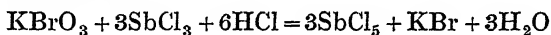
⁷ Vortmann and Metz, *Zeitsch. anal. Chem.*, 1905, 44, 526. See also Manchot, Grassl and Schreiberger, *Zeitsch. anal. Chem.*, 1925, 67, 177.

⁸ Bunsen, *Annalen*, 1858, 106, 3; 1878, 192, 316; Brunck, *Zeitsch. anal. Chem.*, 1895, 34, 171; Rössing, *ibid.*, 1902, 41, 9; Henz, *loc. cit.*; Baubigny, *Compt. rend.*, 1897, 124, 499.

as trioxide, oxidising this precipitate with nitric acid and igniting the residue carefully at 800° C.

In the presence of sodium potassium tartrate, and in faintly acid solution, pyrogallol¹ will precipitate antimony quantitatively.²

Volumetric Methods.³—(a) *Potassium Bromate Method.* In this method, tervalent antimony is oxidised to quinquevalent by the action of potassium bromate :—



The substance containing antimony is dissolved in concentrated hydrochloric acid to which bromine has been added. Excess of bromine is removed by boiling, and the solution reduced by the addition of sodium sulphite solution. The hot solution is then titrated with standard potassium bromate solution until the colour of methyl orange is destroyed. The presence of calcium, magnesium and ammonium salts in quantity tends to give high results, while excess of copper obscures the end-point. If copper is present in any quantity, it is advisable to remove it before estimating the antimony.⁴ Solutions containing antimony in the quinquevalent condition may be completely reduced by mercury in the presence of 3 to 4*N* HCl. The reduction should be carried out in an atmosphere of carbon dioxide. The antimony may then be estimated in such solutions by the bromate method.⁵

(b) *Potassium Iodide Method.* In this method the sample is dissolved in hydrochloric acid to which a little potassium chlorate has been added. Excess of chlorine is removed and potassium iodide added; the liberated iodine is then titrated with a standard solution of sodium thiosulphate.

(c) *Iodine Method.* The solution is made in hydrochloric acid; tartaric acid is added and the mixture neutralised with sodium carbonate. The solution is now made faintly acid, a saturated solution of sodium bicarbonate is added and the mixture is titrated with standard iodine solution.⁶

Other volumetric methods have been suggested involving the use of the following solutions: potassium permanganate,⁷ potassium dichromate,⁸ cerium sulphate⁹ and titanium chloride.¹⁰ Chloramine-T (sodium *p*-toluenesulphonchloramide) may also be employed either for potentiometric or visual titration of antimony.¹¹ A hydrochloric acid

¹ Feigl, *Zeitsch. anal. Chem.*, 1924, 64, 41.

² See also Wenger and Paraud, *Ann. Chim. anal.*, 1923, [2], 5, 230; Darling, *Chem. Eng.*, 1919, 27, 11, 63; *Chem. Zeit.*, 1919, ii, 890; 1920, ii, 750; Cohen and Morgan, *Analyst*, 1909, 34, 3.

³ Schmidt, *Chem. Zeit.*, 1910, 34, 453.

⁴ Györy, *Zeitsch. anal. Chem.*, 1893, 32, 415; Duncan, *Chem. News*, 1907, 95, 49; Nissenon and Siedler, *Chem. Zeit.*, 1903, 27, 749; Rowell, *J. Soc. Chem. Ind.*, 1906, 25, 1181; Nikasono and Inoko, *J. Chem. Soc. Japan*, 1926, 47, 20; Preschar, *Pharm. Zentr.-h.*, 1924, 65, 61; Zintl and Wattenberg, *Ber.*, 1923, 56 B, 472; Jarviness, *Zeitsch. anal. Chem.*, 1923, 62, 184; Evans, *Analyst*, 1932, 57, 554.

⁵ McCay, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 1.

⁶ Brukl, *Mikrochemie*, 1923, i, 54; Kolb and Formhals, *Zeitsch. anorg. Chem.*, 1908, 58, 202; Szebellédy, *Zeitsch. anal. Chem.*, 1930, 81, 36.

⁷ Collenberg and Bakka, *Zeitsch. anal. Chem.*, 1923, 63, 229; Knop, *ibid.*, 1923, 63, 81; Muck, *Chem. Zeit.*, 1922, 46, 790.

⁸ Fleyscher, *J. Amer. Chem. Soc.*, 1924, 46, 2725.

⁹ Furman, *ibid.*, 1932, 54, 4235.

¹⁰ Oliveris, *Ann. chim. applicata*, 1931, 21, 211.

¹¹ Tomicek and Sucharda, *Casopis Českoslov Lékarnictva*, 1931, 11, 285, 309, 320.

solution is used, with, in the case of visual titration, methyl red as indicator.

Electrolytic Titration of antimony ¹ may be carried out in a boiling solution in dilute hydrochloric acid containing hydroxylamine hydrochloride. The initial current should be 3.20 amperes at a pressure of 2 volts.

Electrolytic Methods.—The quantitative electrodeposition of antimony from acid solutions presents considerable difficulties, but the method has been employed for the estimation of the metal.² Solutions of sodium or ammonium thioantimonite or thioantimonate are more usually employed. The presence of polysulphides interferes seriously with the deposition, but their influence may be minimised by the addition of sodium sulphite ³ or potassium cyanide.⁴

Microanalytical Methods for antimony have also been described.⁵

¹ Grosset, *Bull. Soc. chim. Belg.*, 1933, 42, 269.

² Lukas and Jilek, *Chem. Listy*, 1926, 20, 63, 130, 170; Schleicher, Toussaint and Troquay, *Zeitsch. anal. Chem.*, 1926, 69, 39; Schock and Brown, *Eighth Intern. Cong. App. Chem.*, 1912, 21, 81.

³ Lecrenier, *Chem. Zeit.*, 1889, 13, 1219.

⁴ Fischer, *Ber.*, 1903, 36, 2048; *Zeitsch. anorg. Chem.*, 1904, 42, 363; Hollard, *Bull. Soc. chim.*, 1900, [3], 23, 292; Henz, *Zeitsch. anorg. Chem.*, 1903, 37, 31. Also Ost and Klapproth, *Zeitsch. angew. Chem.*, 1900, 13, 828; Foerster and Wolf, *Zeitsch. Elektrochem.*, 1907, 13, 205; Dormaar, *Chem. Weekblad*, 1907, 4, 55; Scheen, *Zeitsch. Elektrochem.*, 1908, 14, 257; Cohen, *Zeitsch. Elektrochem.*, 1908, 14, 301; Mazzucchelli and Tonini, *Atti R. Accad. Lincei*, 1923, [5], 32, ii, 290; Lassieur, *Compt. rend.*, 1923, 177, 263; Parodi and Mascazzini, *Zeitsch. anal. Chem.*, 1879, 18, 587; Luckow, *ibid.*, 1880, 19, 13; Classen and Reiss, *Ber.*, 1881, 14, 1629; 1884, 17, 2474; 1885, 18, 408; 1894, 27, 2074.

⁵ Ordosen and Ressay, *Bull. Soc. chim.*, 1923, [5], 33, 991; Brukl, *loc. cit.*; Sjollem, *Chem. Weekblad*, 1908, 5, 11; Schoorl, *Zeitsch. anal. Chem.*, 1908, 47, 367.

CHAPTER III.

BISMUTH AND ITS ALLOYS.

Symbol, Bi. Atomic Number, 83. Atomic Weight, 209.00 (O = 16).

Occurrence.—Although numerous minerals containing bismuth have been described, very few occur in sufficient quantity to be of economic importance. In general they occur in metalliferous veins associated with ores of cobalt, nickel, lead, zinc, tin, silver, etc. The more important ores are those containing *native bismuth*, *bismuthinite* or *bismuth glance*, Bi_2S_3 , *tetradymite* (sulphide and telluride of bismuth), *bismite* or *bismuth ochre*, Bi_2O_3 , and *bismutite*, $\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$. Deposits occur in many parts of the world, those of Bolivia being the most productive on account of the bismuth minerals in the mountain of Tazna situated in that country.¹ The deposits in Germany,² Czechoslovakia and Hungary are mainly of historical importance. Deposits have also been found in Spain.³ Bismuth-bearing minerals have so far been found only in small quantities in the British Empire, but attempts have been made to develop those of Australia. Native bismuth and bismuthinite have been found in the wolfram- and cassiterite-bearing veins of Lower Burma.⁴ The compositions of some minerals from Vaskő (Hungary) are given in the following table :—⁵

**COMPOSITION OF SOME BISMUTH MINERALS
FROM HUNGARY.**

	Bismuthinite, Bi_2S_3 .		Cosalite, $\text{Pb}_2\text{Bi}_2\text{S}_5$ or $2\text{PbS} \cdot \text{Bi}_2\text{S}_3$.	Rezbanyite, $\text{Cu}_2\text{Pb}_2\text{Bi}_{10}\text{S}_{19}$ or $\text{Cu}_2\text{S} \cdot 3\text{PbS} \cdot 5\text{Bi}_2\text{S}_3$.	
Bismuth . . .	80.04	76.74	41.75	59.28	59.22
Copper . . .	0.57	0.93	3.41	4.17	4.09
Silver	0.32
Lead . . .	0.69	3.29	37.68	18.38	18.10
Iron . . .	0.40	0.11	0.68	0.46	0.42
Sulphur . . .	18.46	18.62	15.92	17.85	17.86
Silica	0.43	0.12
Total . . .	100.16	100.12	99.76	100.14	99.81

¹ Ahlfield, *Zeitsch. prakt. Geol.*, 1932, 40, 119. ² Kühne, *Chem. Erde*, 1932, 7, 503.

³ *Mining Journal, Annual Review Number*, 1930, 28.

⁴ Pascoe, *Records Geol. Survey India*, 1930, 64, 344.

⁵ Koch, *Matematik. es Természettudományi Értesítő*, 1930, 47, 219, 227; *Centr. Mineral. Geol.*, 1930, A, 49.

MINERALS CONTAINING BISMUTH.

Name.	Proximate Formula or Composition.	Hardness (Mohs' Scale).	Density.	Crystalline Form.	Locality.	Literature.*
Native bismuth .	Bi	2 to 2.5	9.7 to 9.8	See under "Metal," p. 130.	Saxony, Bohemia, Scandinavia, Bolivia, Australia	1, 2, 3, 4, 5, 6.
Bismuthinite .	Bi ₂ S ₃ (Analysis [2], Bi 76.51 Sb 3.58 S 20.07)	2	7.4	Rhombic: $a : b : c =$ 0.9862 : 1 : 1.0463 $a = 11.13$ A. $b = 11.27$ A. $c = 3.97$ A. Four molecules per unit cell (See p. 196)	Saxony, Bohemia, Scandinavia, Bolivia, Australia	5, 9, 12, 13, 14, 15, 16, 17, 18, 19, 20, 55, 56.
Cuprobismutite .	3Cu ₂ S.4Bi ₂ S ₃	..	6.3 to 6.4	..	Colorado	29.
Emplectite .	Cu ₂ S.Bi ₂ S ₃	2	6.3 to 6.5	Rhombic: $a = 6.12$ A. $b = 3.89$ A. $c = 14.61$ A.	Saxony, Wurttemberg, Hungary, Norway, Chile	30, 57.
Klaprotholite .	3Cu ₂ S.2Bi ₂ S ₃	2.5	4.6	Rhombic	Black Forest	..
Wittichenite .	3Cu ₂ S.Bi ₂ S ₃	3.5	5 to 6	Rhombic	Baden	30, 31.
Aikinite .	3(Pb, Cu) ₂ S.Bi ₂ S ₃	2.0 to 2.5	6.1 to 6.8	Rhombic	Urals	..
Matildite .	Ag ₂ S.Bi ₂ S ₃	..	6.9	Prismatic	Peru, Colorado	..
Schirmerite .	3(Ag ₂ , Pb) ₂ S.2Bi ₂ S ₃	Soft	6.7	Massive; finely granular	Colorado	..
Schepbachite .	PbS.Ag ₂ S.Bi ₂ S ₃	3.5	6.4	Rhombic (?)	Baden	..
Galenobismutite .	PbS.Bi ₂ S ₃	3.4	6.9	Columnar, also mas- sive	Sweden	16, 17, 21.

* Where no reference is given, see J. D. and E. S. Dana, *loc. cit.*

Name.	Proximate Formula or Composition.	Hardness (Mohs' Scale).	Density.	Crystalline Form.	Locality.	Literature.*
Chiviatite . . .	$2\text{PbS} \cdot 3\text{Bi}_2\text{S}_3$..	6.9	Foliated massive; resembling bismuthinite	Peru	22.
Rezbanyite . . .	$\text{Cu}_2\text{S} \cdot 3\text{PbS} \cdot 5\text{Bi}_2\text{S}_3$..	6.1 to 6.4	Massive; finely granular	Hungary	23.
Cosalite . . .	$2\text{PbS} \cdot \text{Bi}_2\text{S}_3$	2.5 to 3	6.4 to 6.7	Rhombic: $a:b:c = 0.91874:1:1.4601$	Hungary, Sweden, Mexico, Colorado	11, 24.
Lillianite . . .	$3\text{PbS} \cdot \text{Bi}_2\text{S}_3$	Massive	Sweden, Colorado	11, 24.
Beegerite . . .	$6\text{PbS} \cdot \text{Bi}_2\text{S}_3$..	7.3	..	Colorado	25.
Bismutoplagonite . . .	$5\text{PbS} \cdot 4\text{Bi}_2\text{S}_3$	2.8	5.35	Fibrous	Montana	2, 26, 27.
Platynite. . . .	$\text{PbS} \cdot \text{Bi}_2\text{S}_3$	2 to 3	7.98	..	Sweden	28.
Kobellite. . . .	$2\text{PbS} \cdot (\text{Bi}, \text{Sb})_2\text{S}_3$	2.5 to 3.0	6.3	Massive (resembling stibnite)	Sweden, Colorado	..
Histritite	$5\text{CuFeS}_2 \cdot 7\text{Bi}_2\text{S}_3 \cdot 2\text{Sb}_2\text{S}_3$	2	..	Rhombic	Tasmania	32.
Eichbergite . . .	$(\text{Cu}, \text{Fe})_2\text{S}_3 \cdot 3(\text{Bi}, \text{Sb})_2\text{S}_3$	> 6	5.36	..	Austria	33.
Kallitite	NiBiS	Massive	..	34.
Guanajuatite . . .	Bi_2Se_3 [or $\text{Bi}_2(\text{S}, \text{Se})_3$]	2.5 to 3.5	6.2 to 6.6	Rhombic (isomorphous with stibnite)	Mexico	..
Silaonite	Mixture of Bi_2Se_3 and native Bi	2.75	6.44	Massive	Mexico	..
Seleniferous bismuthinite	$4\text{Bi}_2\text{S}_3 \cdot \text{Bi}_2\text{Se}_3$	Laminated masses; resembling tetradymite	Mexico	41.
Joseite	Bi and Te (with some S and Se)	Soft	7.9	..	Brazil	35.

* Where no reference is given, see J. D. and E. S. Dana, *loc. cit.*

Name.	Proximate Formula or Composition.	Hardness (Mohs' Scale).	Density.	Crystalline Form.	Locality.	Literature.*
Tetradymite .	$2\text{Bi}_2\text{Te}_3 \cdot \text{Bi}_2\text{S}_3$	1.5 to 2.0	7.2 to 7.6	Rhombohedral: $a : c = 1 : 1.5871$	Scandinavia, United States	36.
Ornetite .	Bi_6TeS_4	2	6.8	37, 38, 58.
Grunlingite .	Bi_4TeS_4	..	7.3	Rhombohedral (resembling tetradymite)	Cumberland	38.
Wehrite .	Bi and Te (with some S and Ag)	1.2	8.4	..	Hungary	..
Topalpite .	$3\text{Ag}_2(\text{S}, \text{Te}) \cdot \text{Bi}_2(\text{S}, \text{Te})_3$..	7.8	..	Mexico	..
Von Dieckrite .	Telluride of Ag and Bi	Colorado	39.
Weibullite .	$2\text{PbS} \cdot \text{Bi}_4\text{S}_3\text{Se}_3$	3	6.97	..	Sweden	40.
Goldfieldite .	$5\text{Cu}_2\text{S} \cdot (\text{Sb}, \text{Bi}, \text{As})_2(\text{Se}, \text{Te})_3$	3.0 to 3.5	Nevada	40.
Bismite (Bismuth ochre)	Bi_2O_3	Very soft	4.4	Earthy; massive	Saxony, Bohemia, Siberia, United States	1, 5, 7, 8, 9.
Bismutite .	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$	Very soft	6.3 to 7.3	Earthy; pulverulent; amorphous	Saxony, Bohemia, Transvaal, New South Wales	5, 9, 10.
Basobismutite .	$2\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$	Siberia	3, 11.
Bismutosphærite .	$\text{Bi}_2(\text{CO}_3)_3 \cdot \text{Bi}_2\text{O}_3$	3 to 3.5	7.3	Spherical forms, radiated structure	Saxony, Mexico	..
Montanite .	$\text{Bi}_2\text{O}_3 \cdot \text{TeO}_3 \cdot 2\text{H}_2\text{O}$	Earthy	Montana, New South Wales	48.
Eulytite .	$2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$	4.5	6.1	Tetrahedral	Saxony	..

* Where no reference is given, see J. D. and E. S. Dana, *loc. cit.*

Name.	Proximate Formula or Composition.	Hardness (Mohs' Scale).	Density.	Crystalline Form.	Locality.	Literature.*
Agricolite . . .	$2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$	Soft	..	Monoclinic	Saxony	42.
Pucherite . . .	$\text{Bi}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$	4	6.25	Rhombic : $a : b : c =$ 0.5327 : 1 : 2.3357	Saxony	8, 43.
Rhagite . . .	$5\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	5	6.82	..	Saxony	44.
Arsinobismite . .	$2\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$..	5.7	..	Utah	45.
Walpurgite . . .	$5\text{Bi}_2\text{O}_3 \cdot 3\text{UO}_3 \cdot 2\text{As}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$	3.5	5.76	Triclinic	Saxony	46.
Mixite . . .	Basic arsenate of Cu and Bi	3 to 4	3.79	Slender acicular crystals	Joachimsthal, Wittichen, Utah	47.
Uranosphærite . .	$\text{Bi}_2\text{O}_3 \cdot 2\text{UO}_3 \cdot 3\text{H}_2\text{O}$	2.3	6.36	..	Saxony	46.
Koehnlinite . . .	$\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$	Rhombic	Saxony	53, 54.
Bismutotantalite .	$\text{Bi}_2\text{O}_3 \cdot (\text{Ta}, \text{Nb})_2\text{O}_6$	5 to 5.5	> 8	Rhombic $a : b : c =$ 0.7813 : 1 : 0.8522	Uganda	59.
Hancoecornite . .	$(\text{Ni}, \text{Co})_7(\text{S}, \text{Bi}, \text{Sb})_8$ [Bi 23 to 35 per cent.]	5	6.4	Prismatic	Prussia	49.
Bismuth-skutterudite	$\text{Bi}_2\text{As}_2\text{S}_2\text{Co}_2\text{Ni}_2\text{Fe}$ [Bi 4.4 per cent.]	50.
Bismutosmaltite .	$\text{Co}(\text{As}, \text{Bi})_2$ [Bi 20 per cent.]	6	6.92	..	Saxony	51.
Badenite . . .	$[\text{Co}, \text{Ni}, \text{Fe}]_2[\text{As}, \text{Bi}]_3$..	7.1	..	Roumania	52.

* Where no reference is given, see J. D. and E. S. Dana, *loc. cit.*

LITERATURE (MINERALS).

1. Castro Barcos, *Bol. R. Soc. Española Hist. Nat.*, 1921, 21, 291.
2. Ball, *Trans. Inst. Mining and Metallurgy*, 1922, 31, 304.
3. Sushchinski, *Bull. Acad. Sci. Petrograd*, 1917, [6], 11, i, 507; Nenadskinski, *ibid.*, p. 447.
4. Rose, *Abhandlungen K. Akad. Wiss. Berlin*, 1849, 90; *Pogg. Annalen*, 1849, 77, 144.
5. Carnot, *Compt. rend.*, 1874, 79, 302, 477.
6. Burkart, *Jahrbuch für Mineralogie*, 1874, 29.
7. Schaller, and Ransome, *Amer. J. Sci.*, 1910, [4], 29, 173.
8. Schaller, *J. Amer. Chem. Soc.*, 1911, 33, 102.
9. Brown, *Bull. Indian Industry and Labour*, 1921, No. 6, 1.
10. Breithaupt, *Pogg. Annalen*, 1841, 53, 627.
11. Laeoxis, *Bull. Soc. franc. Min.*, 1918, 41, 180.
12. Sharp, *Mining Mag.*, 1918, 18, 280.
13. Maclean, *Mining Mag.*, 1917, 16, 245.
14. Russell, *J. Miner. Soc.*, 1924, 26, 301.
15. Arduini, *Rend. Accad. Lincei, Roma*, 1915, [5], 24, [2], 249.
16. Zealley, *Proc. Rhodesta Sci. Assoc.*, 1917, 16, 17.
17. Wagner, *Mém. Geol. Surv. S. Africa*, 1921, No. 16.
18. Baker, *Trans. Amer. Inst. Min. Met. Eng.*, 1922, 66, 42.
19. Harwood, *J. Miner. Soc.*, 1925, 20, 299.
20. Lindroth, *Geol. For. Forh.*, 1924, 46, 168.
21. Shannon, *J. Wash. Acad. Sci.*, 1921, 11, 298.
22. Rammelsberg, *Pogg. Annalen*, 1853, 88, 320.
23. Frenzel, *Min. Mitth.*, 1883, 5, 175.
24. Walker, *Univ. Toronto Studies, Geol. Surv.*, 1921, No. 12, 5.
25. Koenig, *Amer. Chem. J.*, 1881, 2, 379.
26. Shannon, *Proc. U. S. Nat. Museum*, 1920, 58, 589.
27. Shannon, *Amer. J. Sci.*, 1920, [4], 49, 160.
28. Flink, *Ark. Kemi. Min., Geol.*, 1916, 3, No. 35, 1.
29. Hillebrand, *Amer. J. Sci.*, 1884, 27, 365.
30. Frlwosznik, *Oster. Zeitsch. Berg. Huttenwesen*, 1910, 58, 713.
31. Pound, *Chem. Eng. Mining Review*, 1924, 16, 280.
32. Petterd, *Proc. Roy. Soc. Tasmania*, 1902, 18.
33. Grosspietsch, *Zentral. Kryst. Min.*, 1911, 433.
34. Laspeyres, *Zentral. Kryst. Min.*, 1891, 19, 12.
35. Rickard, *Eng. Mining J.*, 1922, 114, 708, 752, 972.
36. Genth, *Amer. J. Sci.*, 1856, [2], 19, 16.
37. Piña de Rabes, *Anal. Fis. Quim.*, 1919, 17, 83; 1920, 18, 335.
38. Muthmann and E. Schroder, *Zeitsch. Kryst. Min.*, 1897, 29, 144.
39. Cunnenge, *Bull. Soc. min.*, 1899, 22, 25.
40. Ransome, *U. S. Geol. Surv.*, 1909, Prof. Paper 66.
41. Genth, *Amer. J. Sci.*, 1891, 41, 402.
42. Frenzel, *Jahrb. Miner.*, 1873, 791, 917; 1874, 686.
43. Frenzel, *J. prakt. Chem.*, 1871, 4, 227, 361.
44. Weisbach, *Jahrb. Miner.*, 1874, 302.
45. Meuss, *Amer. J. Sci.*, 1916, [4], 41, 127.
46. Weisbach, *Jahrb. Miner.*, 1871, 870; 1873, 315; 1877, 1.
47. Schrauf, *Zeitsch. Kryst. Min.*, 1879, 4, 277.
48. Genth, *Amer. J. Sci.*, 1868, 45, 318.
49. Scheib, *Zeitsch. Geol. Ges.*, 1888, 40, 611.
50. Staudenmann, *Zeitsch. Kryst. Min.*, 1892, 20, 468.
51. Frenzel, *Mineralogische und petrographische Mittheilungen*, 1896, 16, 524.
52. Poni, *Min. Roumanie*, 1900, 17.
53. Schaller, *J. Wash. Acad. Sci.*, 1914, 4, 351.
54. Schaller, *Bull. U. S. Geol. Survey*, 1916, 610, 10.
55. Peacock, *Zeitsch. Kryst.*, 1933, 86, 205.
56. Hofmann, *Zeitsch. Kryst.*, 1933, 86, 223.
57. Hofmann, *Zeitsch. Kryst.*, 1933, 84, 177.
58. Garrido, *Anal. Fis. Quim.*, 1932, 31, 99.
59. Wayland, *Mining Mag.*, 1932, 9, 90, 151; Wayland and Spencer, *Mineralog. Mag.*, 1929, 22, 185.

An examination of the geological formation of the deposits in South America¹ suggested that as native bismuth was found in the upper oxidised portions of the deposit, it should be regarded as of secondary formation, the primary material being bismuthinite.

Details of some of the more important bismuth minerals are given in the tables on pages 120–123, in which the various minerals are grouped together according to their composition. The formulæ are included to give some indication of the composition, and do not necessarily represent definite chemical compounds.²

Early History.—Apparently the first mention of bismuth as a true metal was made by Agricola in the sixteenth century;³ he describes it as a form of lead and outlines a process of extraction by liquation. Bismuth was probably known at a much earlier date, but as it was frequently referred to as *marcasite*—a name used for many different materials—the early history is confused. Paracelsus in the early sixteenth century regarded bismuth as a semi-metal. It was found associated with ores of tin in Saxony, and during extraction bismuth and tin were melted together, the tin thus becoming brittle and hard. Reference to the discovery of bismuth in Europe was made by a South American priest in a report prepared by him on the metal resources of South America.⁴ He wrote: "Bismuth was discovered a few years ago, in the Sudnos Mountains of Bohemia; it is a metal somewhat like a cross between Tin and Lead, without being either of the two."

The metal appears to have been used chiefly in the manufacture of pewter, the addition of bismuth making the metal more sonorous.

The chemistry of bismuth and its compounds was investigated by Lemery,⁵ Pott,⁶ Geoffroy,⁷ Bergmann,⁸ Davy,⁹ Lagerhjelm,¹⁰ Muir and his collaborators, and others.

The origin of the name is not known with certainty. It has been derived conjecturally from Arabic and from Persian, but it is possibly of German origin, connected with a miners' term *wis mat* (weisse masse) meaning "white mass."¹¹

Extraction.—Formerly bismuth was extracted principally from

¹ Kittl, *Rev. Minera Soc. Argentina Minera Geol.* (Buenos Aires), 1930, 2, 1.

² For further mineralogical data and analysis, see Dana, "*A System of Mineralogy*" (London and New York), 6th Ed., 1899; *Appendix I*, 1899; *Appendix II*, 1909; *Appendix III*, 1919. The economic aspect is discussed by Allen, "*Monograph on Mineral Resources with Special Reference to the British Empire, No. 18, Bismuth Ores*" (London), 1925. A bibliography is attached.

³ Agricola, "*De re metallica*," Basilæ, 1558, 439; translated by Hoover (London), 1912; "*De natura fossilium*," Basilæ, 1558, 337. See also Matthesius, *Berg-Postell*, Nürnberg, 1562, 395; Libavius, "*De natura metallorum*," Francofurti, 1600.

⁴ Barba, "*El Arte de los Metales*" (Spain), 1640; translation by Douglas and Mathewson (New York), 1923, p. 55.

⁵ Lemery, "*Cours de Chimie*" (Paris), 1675.

⁶ Pott, "*Observationum et animadversionum chymicum de wismuths*" (Berolini), 1739.

⁷ Geoffroy, *Mém. Acad.*, 1753, 296.

⁸ Bergmann, "*De mineralium docimasia lumida*" (Upsala), 1780.

⁹ Davy, *Phil. Trans.*, 1812, 102, 169.

¹⁰ Lagerhjelm, *Ann. Chim. Phys.*, 1818, [1], 94, 161. See also Kopp, "*Geschichte der Chemie*" (Braunschweig), 1843 to 1847, 4, 110; Lippmann, "*Die Geschichte des Wismuth zwischen 1400 und 1800*" (Berlin), 1930. For an historical account of the use of bismuth in pharmacy, see Dyson, *Pharm. J.*, 1928, 120, 242.

¹¹ von Lippmann, "*Entstehung und Austretung der Alchemie*" (Berlin), 1919, p. 642; Hintze, "*Handbuch der Mineralogie*" (Leipzig), 1904, 1, 123; Hoffmann, *Neues Jahrb. Min.*, 1878, 291; von Kobell, "*Geschichte der Mineralogie*" (München), 1864, 604; Ruland, "*Lexicon alchemie*" (Francofurti), 1612; Matthesius, *loc. cit.*

native ores by the process of liquation. The ore was heated in inclined cylindrical furnaces and the molten bismuth allowed to flow away from the gangue. This crude bismuth was afterwards refined by an oxidising fusion, sometimes followed by poling. As native ores are, however, always associated with oxide or sulphide minerals, or both, neither of which can be treated satisfactorily by liquation, the process is now obsolete.

Bismuth ores do not occur commonly in sufficient quantities to justify direct treatment, but in such cases the main principles underlying the extraction are, firstly, the maintaining of a low temperature on account of the volatility of the metal, and secondly, the use of fluxes suitable for the formation of a fusible slag of a sufficiently low density to enable the metal to separate. The operation may be carried out either in crucibles or in reverberatory furnaces. (1) In the case of oxide ores—which are comparatively unimportant—charcoal or other form of carbon is used as the reducing agent, the fluxes being sodium carbonate, lime and oxide of iron or oxide of manganese. (2) In the case of sulphide ores, particularly if associated with sulphides of arsenic and antimony, the ore is first roasted; arsenic and antimony are thus converted into oxides, partly volatilised and partly removed as scum, while bismuth is converted into a mixture of oxide and sulphate. Reduction to metal is carried out as for oxide ores with the addition of a little iron to remove sulphur. In Bolivia, where the sulphide ore is sufficiently rich and plentiful to be of economic value, smelting with iron is practised, either with or without a preliminary roasting. If there is a preliminary roasting, some bismuth is liable to be converted into bismuth sulphate, which ultimately will tend to pass into a matte. The fusion is carried out in crucibles and reverberatory furnaces, the fused products consisting of crude metallic bismuth, a matte containing copper with 5 to 8 per cent. bismuth, and slag. The matte is subsequently treated in a similar manner until its bismuth content is reduced to 2 to 3 per cent. Both metal and final matte are then refined.¹ The roasting of bismuth sulphide ores presents some difficulty, as the elimination of sulphur is usually incomplete unless either an excess of oxide is present, or special precautions are taken.²

The crude metal obtained in this manner may be refined by an oxidising fusion which removes lead and other easily oxidised metals; the addition of bismuth sulphide assists in the removal of copper as sulphide. The resulting metal is then poled. Frequently bismuthyl chloride is used as a flux in this refining process. A considerable quantity of crude bismuth, however, is converted directly into pharmaceutical products, and for this purpose wet methods are usually employed. Electrolytic refining processes are now more general for the purpose of obtaining pure metallic bismuth (see p. 146).

As has been mentioned, in most localities bismuth ores are associated with ores of other metals, notably lead, tin,³ copper, nickel, cobalt, antimony, arsenic, gold and silver. From these ores the bulk of the world's supply is now obtained, and the method adopted for the extraction of the bismuth depends to a large extent upon the nature of the

¹ Schnabel (translated by H. Louis), "*Handbook of Metallurgy*" (London), 2nd Ed., 1907, 2, 455; Gowland, "*The Metallurgy of the Non-Ferrous Metals*" (London, 1914), p. 466; Frick, *Metal and Erz*, 1928, 25, 550.

² Schenk and Speckmann, *Zeitsch. anorg. Chem.*, 1932, 206, 378; Kohlmeyer, *German Patent*, 1930, 554337; Schoeller, *J. Soc. Chem. Ind.*, 1915, 34, 6. See also p. 198.

³ "*Mineral Resources of the United States of America*," 1928, Part 1, A 18.

associated minerals, although in some cases the ores may be concentrated by the usual mechanical processes and the bismuth concentrates treated separately. Lead-bismuth ores are usually treated as for the extraction of lead, and the crude product subsequently desilverised by the Parkes process; much of the bismuth is retained in the desilverised lead. This is then subjected to the Tredinnick-Pattinson process—a modification of the Pattinson process for the desilverising of lead—whereby the bismuth is concentrated in a small quantity of lead.¹ The bismuth-lead alloy is then treated by the Betts electrolytic process.² In this process the electrolyte is composed of an acid solution of lead fluosilicate containing free hydrofluosilicic acid; the cells are of concrete with a lining of asphalt and are arranged in cascade, there being usually seven cells in cascade. The general arrangement is similar to that employed for the electrolytic refining of copper. The current density is 1.8 to 1.9 amperes per square decimetre, and the potential drop between electrodes is 0.35 to 0.4 volt at the beginning, rising to 0.65 to 0.70 volt at the eighth day. The electrolyte is made to circulate through the cells. The anodes are composed of crude lead containing 2 per cent. of impurities, including bismuth. Antimony is usually present, and is an advantage, as it adheres to the anode, and during the process forms with lead a protective network which remains in position after the bulk of the lead has been dissolved, thus holding the slime, which can be withdrawn with the used anode. Bismuth is found in these slimes, the treatment of which depends very largely upon their composition. This treatment has not been fully published. In one process the slimes are fused with alkalis under oxidising conditions, with the addition of sodium sulphide if copper is present. Arsenic, lead and copper pass into the slag and the bismuth, with gold and silver, is cast into anodes.³ In a second process if gold and silver are present these are removed first, followed by antimony, which is partly converted into lead antimonite slag. By a further oxidation fusion copper is oxidised, and copper oxide and bismuth collect as a slag, from which the bismuth can be obtained electrolytically.⁴ In the electrolytic refining of the slimes, the electrolyte is either a solution of bismuth methyl sulphate (4 per cent.) containing methyl hydrogen sulphate (10 per cent.), or a solution of bismuth chloride with sufficient hydrochloric acid (10 per cent.) to prevent hydrolysis.⁵ In the latter case the current density is 1.5 to 3.8 amperes per square decimetre and the potential drop 0.5 to 1 volt.⁶

Many other processes have also been suggested for the recovery of bismuth both from ores and alloy residues.⁷

¹ Newnam, *Trans. Amer. Inst. Min. Eng.*, 1917, 57, 584.

² Betts, *U.S. Patent*, 1902, 713277; "Lead Refining by Electrolysis" (New York), 1908; Fingland, *Trans. Amer. Electrochem. Soc.*, 1930, 57, 177. See also Schachterle and Riecke, *Metall und Erz*, 1928, 25, 637.

³ Hayward, "An Outline of Metallurgical Practice" (New York, 1929), p. 329.

⁴ Fingland, *loc. cit.*

⁵ Betts, *loc. cit.*, p. 89; van Erckelens, *Eng. Mining J.*, 1931, 132, 160; Donahue, *Trans. Amer. Electrochem. Soc.*, 1930, 57, 153; Kern and Jones, *ibid.*, 255.

⁶ Hayward, *loc. cit.*

⁷ Fingland, Turnbull and McIntyre, *U.S. Patent*, 1931, 1801339; 1932, 1840028; Betterton, *U.S. Patent*, 1932, 1853534, 1853535, 1853536; Smith, *U.S. Patent*, 1932, 1870388, 1870470; Fingland, Turnbull and McIntyre, *Canadian Patent*, 1932, 324755; Cohn, *Trans. Amer. Electrochem. Soc.*, 1931, 59, 107; Kroll, *Metall und Erz*, 1922, 19, 318; *U.S. Patent*, 1922, 1428041; Greene, *U.S. Patent*, 1931, 1821634; Smith, *U.S. Patent*, 1931, 1809871; Smith and Mack, Jun., *U.S. Patent*, 1931, 1816620; Donahue, *U.S. Patent*, 1930, 1778292; Kohlmeier, *German Patent*, 1927, 494454; 1928, 502198.

ANALYSIS OF ANODES OF CRUDE BISMUTH

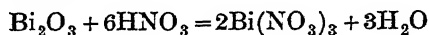
(As used for Electrolytic Refining).¹

	Peru.	Australia.	United States.		Mexico.
Bismuth .	98.37	94.10	90.45	95.03	94.00
Antimony .	4.57	2.62	0.19	Trace	0.11
Arsenic .	..	0.92	0.26	Trace	..
Copper .	2.06	1.94	3.71	2.97	0.48
Lead	1.82	0.87	2.20
Sulphur .	..	0.48	0.99	0.21	..
Iron	1.81	0.45	..
Silver	186.1 oz. per ton	156.1 oz. per ton	3.20

An earlier method for the extraction of bismuth from bismuth-lead ores involved the process of cupellation. Bismuth will not oxidise until all the lead is oxidised; part of it, therefore, during cupellation, will pass into the silver, and part into the final litharge produced. Bismuth may be recovered from the latter by dissolving in hydrochloric acid and precipitating as bismuthyl chloride, which, in turn, may either be used as such, or may be reduced by heating with charcoal and sodium carbonate. Gold and silver may be removed from bismuth by the addition of a little zinc to the molten metal and treating as in the Parkes desilverising process.

Wet processes are seldom used for the extraction of the metal, but are mainly employed for the preparation of medicinal and pharmaceutical products. In general, the ore is dissolved in hydrochloric acid, aqua regia or sulphuric acid, and from the solution bismuth is precipitated by iron. If hydrochloric acid is used as the solvent, bismuthyl chloride is precipitated, and from this the metal is obtained as previously described.² The impure bismuth may be refined by liquation, dissolved in nitric acid, precipitated as basic nitrate, redissolved in nitric acid and precipitated as hydroxide by ammonia; this bismuth hydroxide, after washing and drying, may be reduced by hydrogen. Most pharmaceutical preparations are to-day made from refined bismuth.

The method employed in Norway by the Norsk Hydro-Electrisk Kvaestof Aktieselskab³ involves the treatment of bismuth ores with crude nitric acid obtained by the solution of oxides of nitrogen in water. If the ore contains bismuth trioxide the action is simple neutralisation according to the equation



The action is more complicated when sulphide ores are treated. The ore is first partially roasted, ground finely, and added to the crude nitric

¹ Kern and Jones, *Trans. Amer. Electrochem. Soc.*, 1930, 57, 257.

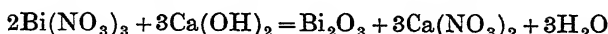
² Hertel, *Metall und Erz*, 1930, 27, 557; I.G. Farbenind. A.G., *German Patent*, 1927, 498921; Guggenheim Bros., *German Patent*, 1928, 503806; Kali-Chemie A.G., *German Patent*, 1929, 544933.

³ Dyson, *Chemical Age*, 1926, 15, 25.

acid. The main reaction may perhaps be represented by the equation



When the acid is almost completely neutralised, the lye is removed, concentrated and poured into milk of lime. Bismuth trioxide is thus precipitated and calcium nitrate remains in solution:



This process is used mainly for the production of salts of bismuth.

Pure bismuth may also be obtained by converting the nitrate into oxide and reducing the oxide by fusion with potassium cyanide. A further purification may be effected by liquation. Bismuth containing less than 0.01 per cent. of impurities (the chief of which is copper) has been obtained.¹ Below are given the upper and lower limits of the impurities present in six samples of bismuth examined spectrographically.²

Copper	0.001 to 0.006 per cent.
Silver	0.006 to 0.046 "
Tellurium	0.000 to 0.004 "
Thallium	0.000 to 0.005 "
Lead	0.002 to 0.061 "
Total					0.009 to 0.122 "

Physical Properties of Bismuth.

It is possible that bismuth can exist in several *allotropic forms*, but the evidence at present available is not conclusive. Transition points have been reported, occurring at 75° C.,³ 112° C. and 116° C.⁴ In addition, it has been suggested that a cubic modification of bismuth exists at temperatures just below the melting point, changing into the hexagonal form at a slightly lower temperature.⁵ No direct evidence has been obtained for the existence of cubic bismuth, but a transformation of this order might possibly afford an explanation of the cracks which are set up during the growth of a single bismuth crystal; evidence for the existence of such cracks is abundant,⁶ but it is more probable that they are due to impurities.⁷ A comparison of the electrical resistance of unannealed bismuth with that of the slowly-cooled metal indicates that a transformation occurs⁸ between 160° and 180° C. Investigation of the thermal and electrical properties of very pure bismuth, containing less than 0.01 per cent. of impurities (consisting of platinum, silver and iron), failed to reveal any transition point at 75° C.

¹ Mylius and Groschuff, *Zeitsch. anorg. Chem.*, 1916, 96, 237. For a general account of the occurrence, extraction, recovery, refining and economics of bismuth, see *U.S. Bureau of Standards*, 1930, Circular No. 382; Strom, *Eng. Mining J.*, 1935, 136, 20.

² Goetz and Focke, *Phys. Review*, 1934, 45, 170.

³ Cohen and Moesveld, *Zeitsch. physikal. Chem.*, 1913, 85, 419; *Chem. Weekblad*, 1913, 10, 656.

⁴ Janecke, *Zeitsch. physikal. Chem.*, 1915, 90, 313.

⁵ Kapitza, *Proc. Roy. Soc.*, 1928, 119 A, 358.

⁶ Schneider, *Phys. Review*, 1928, [2], 31, 251; Boydston, *ibid.*, 1927, [2], 30, 911; Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, 60, 361; 1929, 63, 351; Borelius and Lindh, *Ann. Physik*, 1916, 51, 607.

⁷ Webster, *Proc. Roy. Soc.*, 1931, 133 A, 162.

⁸ Pietenpol and Miley, *Phys. Review*, 1929, [2], 34, 1588.

or near the melting point. The temperature-resistance curve shows no inflections between -190° and 271° C. Photomicrographs failed to show any difference in the structure of bismuth chilled at various temperatures.¹ Evidence derived from the investigation of the thermal expansion of a bismuth single crystal has yielded interesting results with reference to the possible allotropic change at 75° C. When the thermal expansion is determined by ordinary methods there is a definite discontinuity on the temperature-expansion curve at 75° C. No such discontinuity was at first observed when measurements were made on the crystal lattice by X-rays,² but a later investigation³ revealed a small but definite increase in the coefficient of expansion between 70° and 80° C. It is possible, therefore, that an allotropic change does occur at approximately 75° C., but the nature of the change, if it exists, has not been determined. It is probable that another modification of bismuth is obtained at the ordinary temperature by the application of pressure of the order of 25,000 kilograms per sq. cm. Since the transition to this new form is accompanied by a reduction in volume of about 9 per cent., it is deduced that this modification should be formed from the liquid with a contraction of the order of 1 per cent. This new form of bismuth appears to be analogous to the high-pressure modification of ice.⁴

Bismuth is a white metal, having a slight reddish tinge and a brilliant metallic lustre. It is very brittle and can easily be powdered; it can, however, be worked to a very slight extent by very careful hammering. It crystallises in rhombohedra belonging to the hexagonal system⁵

$$a : c = 1 : 1.3085 ; \quad \alpha = 87^{\circ} 34'$$

The examination of bismuth crystals by X-rays indicates that the metal crystallises in the di-hexagonal class of the hexagonal system; the structure is that of a face-centred lattice, the bismuth atoms lying on two interpenetrating face-centred rhombohedral lattices.⁶ The unit rhomb contains eight atoms, the length of the edge lying between 6.52×10^{-8} cm. and 6.57×10^{-8} cm. The length of the edge of unit structure is 3.28×10^{-8} cm. The three edges of the rhombohedron meet in the trigonal axis, and the angle between any two of the edges is $87^{\circ} 34'$. The angles between the faces have been determined. The crystals have perfect cleavage parallel to the (111) plane and perpendicular to the trigonal axis, but the cleavage is not so good parallel to

¹ Schulze, *Zeitsch. Metallkunde*, 1930, 22, 194; *Zeitsch. tech. Physik*, 1930, 10, 16.

² Goetz and Hergenrother, *Phys. Review*, 1932, 40, 643.

³ Jay, *Proc. Roy. Soc.*, 1934, 143 A, 465.

⁴ Bridgman, *Phys. Review*, 1934, [2], 45, 844. For further discussion of the allotropy of bismuth, see Goetz and Hasler, *Phys. Review*, 1930, 36, 1752; Cartwright, *Review Sci. Instruments*, 1932, 3, 73; Tammann and Kohlhaas, *Zeitsch. anorg. Chem.*, 1931, 199, 209; Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1921, 56, 115; Cohen and Moestfeld, *Versl. Akad. Wetensch. Amsterdam*, 1920, 28, 762; Würschmidt, *Jahrb. Min.*, 1917, i, Ref. 2; *Ber. deut. physikal. Ges.*, 1913, 15, 1027; 1914, 16, 799; Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 17, 1236; Curie, *J. Physique*, 1895, 4, 206; Aoyama and Monna, *Sci. Rep. Tohoku Imp. Univ.*, 1934, 23, 52.

⁵ Groth, *Chem. Krystallographie*, 1906, 1, 18, 22; Pushin, *Zeitsch. anorg. Chem.*, 1903, 36, 243; Marchand and Scheerer, *J. prakt. Chem.*, 1883, [2], 27, 193; Stolba, *J. prakt. Chem.*, 1865, 96, 183; Rose, *Pogg. Annalen*, 1849, 77, 143; Quesneville, *J. Pharm.*, 1830, 16, 554.

⁶ Goldschmidt, *Zeitsch. physikal. Chem.*, 1928, 133, 397; Hassel and Mark, *Zeitsch. Physik*, 1924, 23, 269; Ogg, *Phil. Mag.*, 1921, [6], 42, 163; James, *ibid.*, p. 193; Johnsen, *Centr. Min.*, 1916, 385.

the (11 $\bar{1}$) planes. The "atomic diameter," or closest approach of two atoms,¹ is 3.11×10^{-8} cm. Bismuth crystallises from the melt in skeleton rhombohedra of the form indicated.² The structures of spluttered and evaporated bismuth films³ and of electrolytic bismuth⁴ have also been described. Native bismuth probably has not preserved its primary structure.⁵ The spontaneous crystallising power of bismuth has been investigated.⁶ X-rays do not appear to alter the structure of bismuth during crystallisation.⁷ Investigation of the variation of certain physical properties of bismuth with crystal deformation has suggested that a secondary or "mosaic" structure is superimposed upon the lattice, and that this "mosaic" structure, which is perfectly regular, is capable of undergoing deformation without alteration of the crystal lattice itself.⁸

Single crystals of bismuth have been prepared⁹ and their properties examined. On account of their anisotropic nature they have received considerable attention. The different values that have been obtained by different investigators for some of the properties may be due to imperfections in the crystal, for it is claimed that slight strains set up during the growth of a bismuth crystal have a great influence on the orientation of the trigonal axis of the crystal lattice; in addition, as has been mentioned previously, cracks may develop in the crystal at a temperature just below the melting point. The effect of a magnetic field upon the growth of a bismuth single crystal has been examined,¹⁰ and the results of these investigations lend support to the theory of "mosaic" structure.

The density¹¹ of bismuth (D_4^{20}) is 9.80. That of single crystals¹² grown under normal conditions is 9.82 to 9.83; it is affected by the presence of a magnetic field during the growth of the crystal.

The coefficient of thermal expansion (linear)¹³ is 12.98×10^{-6} between

¹ See Bragg, *Phil. Mag.*, 1920, [6], 40, 169.

² For further discussion of crystal structure, see also Jones, *Proc. Roy. Soc.*, 1934, 147 A, 404; Adinolfi, *Rend. Accad. Sci. Napoli*, 1930, [3], 36, 69; Davey, *Phys. Review*, 1925, 25, 753; McKeehan, *J. Franklin Inst.*, 1923, 195, 51.

³ Kahler, *Phys. Review*, 1921, 18, 210. See also Bussem, Gross and Herrmann, *Zeitsch. Physik*, 1930, 64, 537.

⁴ Stillwell and Audrieth, *J. Amer. Chem. Soc.*, 1932, 54, 472; Hirata, *Elec. Review (Japan)*, 1928, 16, 651, 761.

⁵ Carpenter and Tamura, *Bull. Inst. Mining and Metallurgy*, 1928, No. 282.

⁶ Bekier, *Zeitsch. anorg. Chem.*, 1912, 78, 178.

⁷ Kostagni, *Atti R. Accad. Lincei*, 1928, [6], 7, 646; Adinolfi, *ibid.*, 1925, [6], 1, 382; 1928, [6], 8, 381.

⁸ Zwicky, *Proc. Nat. Acad. Sci.*, 1929, 15, 816; Goetz, *Phys. Review*, 1930, 35, 193; Goetz and Hasler, *ibid.*, 1930, 36, 1752; Goetz and Focke, *Phys. Review*, 1931, 37, 1044. See also Stewart and Morrow, *Phys. Review*, 1927, 30, 232.

⁹ von Gomperz, *Zeitsch. Physik*, 1922, 8, 184; Obreimov and Shubnikov, *Trans. Phys. Rech. Lab., Leningrad*, 1925, 100, 21; Shubnikov, *Proc. Acad. Sci. Amsterdam*, 1930, 33, 327; Goetz, *Phys. Review*, 1930, 35, 193.

¹⁰ Tieri and Percies, *Linc. Rend.*, 1921, 30, 464; Goetz and Hasler, *Proc. Nat. Acad. Sci.*, 1929, 16, 646; *loc. cit.*; Goetz, *loc. cit.*; Goetz and Focke, *loc. cit.*; Goetz and Hergenrother, *Phys. Review*, 1932, 40, 137.

¹¹ *International Critical Tables*, 1927, 2, 456. See also Davey, *Phys. Review*, 1924, 23, 292; Endo, *J. Inst. Metals*, 1923, 30, 121; Lowry and Parker, *J. Chem. Soc.*, 1915, 107, 1005; Johnston and Adams, *J. Amer. Chem. Soc.*, 1912, 34, 563; Kahlbaum, Roth and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 294; Marchand and Scheerer, *J. prakt. Chem.*, 1883, [2], 27, 193.

¹² Goetz and Focke, *loc. cit.*

¹³ *International Critical Tables*, 1927, 2, 460; Grüneisen, *Ann. Physik*, 1910, 33, 65. See also Friend and Vallance, *J. Inst. Metals*, 1924, 31, 79 (Discussion); Dorsey, *Phys. Review*, 1907, 25, 88.

-188° and 15° C., and 13.45×10^{-6} between 19° and 101° C. For a single crystal the coefficient ¹ at the ordinary temperature is 13.96×10^{-6} parallel to the trigonal axis, and 10.86×10^{-6} perpendicular to that axis, the mean coefficient ² between 20° and 240° C. being 16.6×10^{-6} parallel to the trigonal axis, and $(12.0 \pm 0.2) \times 10^{-6}$ perpendicular to that axis; between 240° C. and the melting point the coefficient falls off very markedly.³ The effect of a magnetic field upon the coefficient of thermal expansion (linear) of a single crystal has been determined.⁴ The coefficient of thermal expansion (cubical) ⁵ is 39.6×10^{-6} .

The mean compressibility ⁶ is 3.0×10^{-6} for the pressure range between 100 and 500 megabars.⁷ This value decreases at very high pressures. The compressibility of single crystals has also been determined.⁸

The hardness on Mohs' scale ⁹ is 2.5; the Brinell hardness number ¹⁰ (using a 6.35 mm. ball and a load of 40.8 kg. at 15.5° C.) is 7.3.

Young's modulus is 0.82×10^6 kg. per sq. cm., and the tensile strength about 450 kg. per sq. cm.¹¹

The specific heat at the ordinary temperature ¹² lies between 0.03023 and 0.0303, and the variation with temperature is given approximately by ¹³

$$c = 0.030 + 0.000013t$$

(where t is the temperature in degrees Centigrade), but there is an

Temperature, ° C. . . .	27	77	127	177	227	267	272.7 (liq.)	327.2 (liq.)	371.1 (liq.)
Atomic Heat at Constant Pressure	6.15	6.31	6.46	6.60	6.73	6.83	7.217	7.119	6.995
Atomic Heat at Constant Volume	6.08	6.22	6.35	6.48	6.60	6.70

¹ Bridgman, *Proc. Nat. Acad. Sci.*, 1924, 10, 411. See also Fizeau, *Compt. rend.*, 1869, 68, 1125.

² Jay, *Proc. Roy. Soc.*, 1934, 143 A, 465; Goetz and Hergenrother, *loc. cit.*; *Phys. Review*, 1931, 38, 2075.

³ Roberts, *Proc. Roy. Soc.*, 1924, 106 A, 385; Jay, *loc. cit.*

⁴ Kaye and Higgins, *Phil. Mag.*, 1929, [7], 8, 1057.

⁵ Endo, *loc. cit.* See also Kopp, *Pogg. Annalen*, 1852, 86, 156; Matthiessen, *ibid.*, 1867, 130, 50.

⁶ Richards, *J. Amer. Chem. Soc.*, 1915, 37, 1643; Adams, Williamson and Johnston, *ibid.*, 1919, 41, 12. See also Grüneisen, *Ann. Physik*, 1908, 25, 825; Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1923, 58, 166; 1924, 59, 109.

⁷ See p. 18.

⁸ Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, 60, 305.

⁹ Rydberg, *Zeitsch. physikal. Chem.*, 1900, 33, 353.

¹⁰ Hargreaves, *J. Inst. Metals*, 1928, 39, 314.

¹¹ Mallock, *Proc. Roy. Inst. Great Britain*, 1921, 23, 377; *Proc. Roy. Soc.*, 1919, 95 A, 429; Schulze, *Sitzber. Ges. Marburg*, 1903, 80, 94; Voigt, *Wied. Annalen*, 1893, 48, 674. For the mechanical properties of single crystals, see Schmid, *Metallwirtschaft*, 1928, 7, 1011; *Proc. First International Congress of Applied Mechanics*, 1924, 324; Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, 60, 305; *Proc. Nat. Acad. Sci.*, 1924, 10, 411; Georgieff and Schmid, *Zeitsch. Physik*, 1926, 36, 759; Haase and Schmid, *ibid.*, 1925, 33, 413; von Gompertz, *ibid.*, 1922, 8, 184.

¹² Rostagni, *Atti R. Accad. Lincei*, 1928, [6], 7, 649. See also Awberry and Griffiths, *Proc. Phys. Soc.*, 1926, 38, 378; Adinolfi, *Atti R. Accad. Lincei*, 1928, [6], 8, 381; Denizot, *Physikal. Ber.*, 1927, 8, 1584; *Bull. Soc. Amis sci. Poznan*, 1926, 2, 1; Umino, *Sci. Rep. Tohoku Imp. Univ.*, 1926, [1], 15, 597; Iitaka, *ibid.*, 1919, 8, 99; Schimpff, *Zeitsch. physikal. Chem.*, 1910, 71, 257; Kahlbaum, Roth and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 294.

¹³ *International Critical Tables*, 1929, 5, 93.

anomalous increase when the temperature is 20° to 30° C. below the melting point.¹ The *atomic heats* (in calories per gram-atom) at high temperatures are as in table on p. 132. The atomic heats at low temperatures are : ²

Temp., ° C.	Atomic Heat (calories per gram-atom).	Temp., ° C.	Atomic Heat (calories per gram-atom).	Temp., ° C.	Atomic Heat (calories per gram-atom).
-270	0.0102 ³	-161.8	5.674	-64.2	5.974
-253	2.05 ³	-147.9	5.813	-54.2	5.980
-212.2	4.631	-135.8	5.761	-14.9	5.874
-209.6	4.851	-123.8	5.817	- 6.7	6.058
-208.3	4.771	-110.5	5.869	- 0.2	6.083
-201.9	5.040	- 96.2	5.899	+12.3	6.139
-198.4	5.216	- 85.3	5.924	+22.2	6.089
-171.7	5.464	- 74.1	5.976	+25.2	6.104

The metal employed was very pure, and contained no lead, arsenic or antimony. The specific heat of bismuth is increased by chilling, and after exposure to X-rays.⁴

The *melting point*⁵ is usually given as 271° C., but values as low as 269° C. have been recorded. The metal is very susceptible to supercooling, and it has been shown that the degree of supercooling at which the bismuth nuclei begin to recrystallise is definitely related to the degree of superheating to which the metal has been submitted; and also, that the crystal nuclei tend to persist after melting and are only slowly destroyed on superheating.⁶ If a single crystal of bismuth is heated to 10° C. above the melting point, and cooled slowly, the re-formed solid shows the same crystallographic orientation as the original crystal; when heated to a higher temperature, however, and then re-solidified, a random orientation results.⁷ The linear velocity of crystallisation reaches a maximum value of 2 cm. per minute with 2° of supercooling.⁸

The *latent heat of fusion*⁹ is 13 calories per gram.

Bismuth contracts considerably on passing from the solid to the liquid state, the *percentage contraction*¹⁰ being 3.47. The metal further resembles water in that the liquid attains a maximum density at a

¹ Carpenter and Harle, *Proc. Roy. Soc.*, 1932, 136 A, 243.

² Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2720.

³ Keesom and van den Ende, *Proc. Acad. Sci. Amsterdam*, 1931, 34, 210; 1930, 33, 243; van den Ende, *Metallwirtschaft*, 1931, 10, 876.

⁴ Adinolfi, *loc. cit.*

⁵ *International Critical Tables*, 1927, 1, 103. See also Awberry and Griffiths, *loc. cit.*; Endo, *J. Inst. Metals*, 1923, 30, 121; Jänecke, *Zeitsch. physikal. Chem.*, 1931, 156 A, 161; Bigelow and Rykenboer, *J. Phys. Chem.*, 1917, 21, 474; Mylius and Groschuff, *Zeitsch. anorg. Chem.*, 1904, 40, 54.

⁶ Webster, *Proc. Roy. Soc.*, 1933, 140 A, 653.

⁷ Donat and Stierstadt, *Ann. Physik*, 1933, 17, 897.

⁸ Tammann and Rocha, *Zeitsch. anorg. Chem.*, 1933, 216, 17.

⁹ Awberry and Griffiths, *loc. cit.* See also Umino, *loc. cit.*; Iitaka, *loc. cit.*

¹⁰ Goodrich, *Trans. Faraday Soc.*, 1929, 25, 531. See also Endo, *loc. cit.*; Bornemann and Siebe, *Zeitsch. Metallkunde*, 1922, 14, 329; Johnston and Adams, *loc. cit.*; Hess, *Ber. deut. phys. Ges.*, 1906, 3, 403; Toepfer, *Ann. Physik*, 1894, [2], 53, 343; Vincentini, *Atti R. Accad. Lincei*, 1890, [6], 121, 147.

temperature just above the melting point.¹ It is probable, however, that at very high pressures a modification of bismuth exists whose density is greater than that of the corresponding liquid phase (see p.138).

The density of liquid bismuth² is given by

$$D = 10.07 - 0.00125(t - 269)$$

where t is the temperature in degrees Centigrade. Between 420° and 1100° C. the relationship between the specific volume, v_t , and the temperature, t° C., is given by³

$$v_t = 0.1011 + (128 \times 10^{-7})(t - 420)$$

Between 420° and 271° C., however, this relationship does not hold, the specific volume decreasing less rapidly with fall of temperature below 420° C. From this, from a consideration of the effect of bismuth on the melting points of other metals, and from the surface tension, it is calculated that the molecular weight of bismuth is constant at approximately 209 between 420° and 1400° C., increasing sharply above that temperature and attaining a value of 334 at 1500° C. At 2100° C. bismuth again becomes monatomic (see also p. 136).

The specific heat of the liquid⁴ at 369° C. is 0.019.

The surface tension of liquid bismuth has been determined by a number of investigators,⁵ and the more recent results showing the variation with temperature are as follows :

Temp., ° C.	269	300	320	365	400	426	472	583	600	779	802	962	..
σ	378	..	375	371	..	367	365	Hogness.
(dynes	354	..	344	Sauerwald
per cm.)	..	388	380	367	..	353	340	and Drath.
													Birkumshaw.

From his results, Birkumshaw deduces that liquid bismuth is associated. For the *parachor*, calculated from the results of Hogness and Birkumshaw, the values 92.0 and 94.4 have been obtained.⁶ The atomic *parachor*, determined by measurements on covalent compounds, is 80.0; there are thus positive anomalies of 12.0 and 14.4 respectively. Since, if a double bond joins two atoms, the *parachor* (calculated for one atom) will show a positive anomaly of 11.6, it is deduced that, for bismuth in liquid form, the molecule contains two atoms which share four electrons.⁷

The viscosity of liquid bismuth⁸ decreases from about 0.0168 at 300° C. to about 0.01 at 600° C.

¹ Lüdeking, *Ann. Phys. Chem.*, 1888, [2], 34, 21.

² Hogness, *J. Amer. Chem. Soc.*, 1921, 43, 1621. See also Bornemann and Sauerwald, *Zeitsch. Metallkunde*, 1922, 14, 145; Bornemann and Siebe, *ibid.*, 1922, 14, 329; Plüss, *Zeitsch. anorg. Chem.*, 1915, 93, 1.

³ Jouniaux, *Bull. Soc. chim.*, 1932, 51, 677. See also Matsuyama, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1928, 7, 1054; *Sci. Rep. Tohoku Imp. Univ.*, 1929, 18, 19.

⁴ Awberry and Griffiths, *loc. cit.*

⁵ Hogness, *loc. cit.*; Sauerwald and Drath, *Zeitsch. anorg. Chem.*, 1926, 154, 79; Birkumshaw, *Phil. Mag.*, 1927, [7], 3, 1286; Matsuyama, *Sci. Rep. Tohoku Imp. Univ.*, 1927, 16, 555; Smith, *J. Inst. Metals*, 1914, 12, 168; Siedentopf, *Wied. Annalen*, 1897, 61, 235; Quincke, *Pogg. Annalen*, 1869, 138, 141.

⁶ Sugden, "The *Parachor and Valency*" (London, 1930), p. 174.

⁷ See also Jouniaux, *loc. cit.*

⁸ Sauerwald and Topler, *Zeitsch. anorg. Chem.*, 1926, 157, 117. For the viscosity of solid bismuth, see Harris, *Phys. Review*, 1912, 35, 95.

The *boiling point* ¹ lies between 1440° and 1500° C. It varies considerably with pressure, as the following data show :

Pressure (mm.) .	102	257	760	4788	8892
Boiling point (° C.) .	1200	1310	1500	1870	2100

From these data the *latent heat of vaporisation* of bismuth ² is found by calculation to be 42,700 gram-calories per mole. The variation of the *vapour pressure* of bismuth with temperature is given as follows : ³

Temperature (° C.) .	1210	1290	1385	1410	1490
Pressure (mm.) .	63	126	300	406	760

Between 827° and 947° C. the vapour pressure of bismuth may be calculated from the expression ⁴

$$\log_{10} P = -\frac{52.23 \times 195.26}{T} + 8.56$$

where P is the vapour pressure in millimetres and T the absolute temperature.

The vapour of bismuth at 2000° C. is monatomic, ⁵ although at lower temperatures it is possible that both monatomic and diatomic molecules exist. ⁶ It has been stated that the vapour at 851° C. contains 40 per cent. of Bi molecules and 60 per cent. of Bi₂ molecules, ⁷ while at 827° C. approximately 2 per cent. of Bi₃ molecules were detected in addition to Bi and Bi₂. No evidence has yet been obtained for the existence of molecules of different constitution, such as Bi₃, Bi₄ or Bi₈. The heat of dissociation ⁸ of diatomic molecules of bismuth is stated to be 77,100 ± 1200 gram-calories per mole.

Chiefly on account of the anisotropic nature of crystalline bismuth, the thermal, electrical and magnetic properties have received considerable attention.

Bismuth is a poor conductor of heat and of electricity ; the relative *thermal conductivity* ⁹ is 1.8, that of silver being 100. The variation of thermal conductivity with temperature ¹⁰ of solid bismuth is as follows :

¹ Greenwood, *Proc. Roy. Soc.*, 1910, 83 A, 483; 1909, 82 A, 396. See also Ruff and Mugdan, *Zeitsch. anorg. Chem.*, 1921, 117, 147; van Liempt, *ibid.*, 1920, 114, 115; Ruff and Bergdahl, *ibid.*, 1919, 106, 76; von Wartenburg, *Zeitsch. Elektrochem.*, 1913, 19, 482; Greenwood, *ibid.*, 1912, 18, 319; *Zeitsch. physikal. Chem.*, 1911, 76, 484; Krafft and Lehmann, *Ber.*, 1905, 38, 254; Krafft and Bergfeld, *ibid.*, 1905, 38, 257, 1905; Barus, *Amer. J. Sci.*, 1894, [3], 48, 332; Biltz and Meyer, *Ber.*, 1889, 22, 725; Carnelley and Williams, *Chem. News*, 1879, 39, 286. See, however, Leitgeb, *Zeitsch. anorg. Chem.*, 1931, 202, 305.

² Greenwood, *Chem. News*, 1911, 104, 31, 42; *Zeitsch. physikal. Chem.*, 1911, 76, 484.

³ Ruff and Bergdahl, *loc. cit.*

⁴ Ko, *J. Franklin Inst.*, 1934, 217, 173.

⁵ von Wartenburg, *Zeitsch. anorg. Chem.*, 1907, 56, 320.

⁶ Biltz and Meyer, *loc. cit.*

⁷ Zartmann, *Phys. Review*, 1931, [2], 37, 383.

⁸ Wiedemann and Franz, *Pogg. Annalen*, 1853, 89, 497.

¹⁰ Konno, *Phil. Mag.*, 1920, [6], 40, 542.

^{*} Ko, *loc. cit.*

Temperature, ° C.	18	89	160	222	233	256
Thermal conductivity	0.0194	0.0181	0.0170	0.0177	0.0177	0.0183

That of liquid bismuth is :

Temperature, ° C.	286	298	376	484	584
Thermal conductivity	0.0400	0.0418	0.0378	0.0372	0.0369

The conductivity in all the above cases is measured in gram-calories per cm. per sec. per degree Centigrade. It will be observed that the thermal conductivity of solid bismuth decreases to a minimum with rise of temperature, afterwards rising to the melting point; that of liquid bismuth is nearly constant above 300° C., whilst at the melting point there is a very considerable increase. Bismuth differs from most metals in this respect, although antimony also shows a slight increase in thermal conductivity on melting.¹ The effects of pressure² and of a magnetic field³ upon the thermal conductivity have been determined. The thermal conductivities of a single crystal of bismuth are :⁴

Perpendicular to the trigonal axis	0.0221 calories per cm. per sec. per ° C.
Parallel to the trigonal axis	0.0159 „ „ „
Mean value (assuming a random distribution of crystals)	0.0195 „ „ „

The electrical resistance⁵ is 106.5×10^{-6} ohm-cm. at 0° C., and the variation with temperature is given by

$$R = 106.5[1 + 0.00391t + 0.0000058t^2] \times 10^{-6} \text{ ohm-cm.}$$

where t is the temperature in degrees Centigrade. The mean temperature coefficient of resistance between 0° and 100° C. is 4.46×10^{-5} . At the melting point the resistance of solid bismuth is 267×10^{-6} ohm-cm.; that of liquid bismuth at the same temperature is 127.5×10^{-6} ohm-cm.⁶ Bismuth is not superconducting at -268.84°C . The resistance at low temperatures is as follows, being given as a ratio between that at the temperature stated (R) and that at 0° C. (R_0).⁷

¹ For thermal conductivity, see also Jaeger and Diesselhorst, *Wissenschaftl. Abhandl. phys. tech. Reichsanst.*, 1900, 3, 269; Giebe, *Inaugural Dissertation*, Berlin, 1903; *Verh. deut. physikal. Ges.*, 1903, 5, 60; Lorenz, *Wied. Annalen*, 1881, 13, 422, 582.

² Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1922, 57, 77.

³ Ward, *Phil. Mag.*, 1924, [6], 48, 971; Knapp, *Phys. Review*, 1932, 39, 550.

⁴ Kaye and Roberts, *Proc. Roy. Soc.*, 1923, 104 A, 98. See also Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1928, 61, 101; *Proc. Nat. Acad. Sci.*, 1925, 11, 608; Kaye and Higgins, *Phil. Mag.*, 1929, [7], 8, 1056; de Haas and Capel, *Physica*, 1934, 1, 929.

⁵ *International Critical Tables*, 1929, 6, 136. See also Dewar and Fleming, *Proc. Roy. Soc.*, 1897, 60, 72; Shubnikov and de Haas, *Proc. Acad. Sci. Amsterdam*, 1930, 33, 350; Northrup and Seydam, *J. Franklin Inst.*, 1913, 175, 153; Northrup, *Trans. Amer. Electrochem. Soc.*, 1914, 25, 375.

⁶ See also Matsuyama, *Sci. Rep. Tohoku Imp. Univ.*, 1927, 16, 447; *Kinzoku-no-Kenkyu*, 1926, [4], 3, 254; *Trans. Amer. Soc. Steel Treatment*, 1926, 10, 318; Pietenpol and Miley, *Phys. Review*, 1929, 33, 294.

⁷ *International Critical Tables*, 1929, 6, 125. For bibliography, see *ibid.*, p. 134.

ELECTRICAL RESISTANCE OF BISMUTH AT LOW TEMPERATURES.

Temperature, ° C.	$\frac{100R}{R_0}$	Temperature, ° C.	$\frac{100R}{R_0}$
-103.71	63.649	-204.68	36.064
-139.88	52.865	-216.01	33.014
-164.05	46.246	-253.01	22.329
-182.73	41.435	-255.34	21.388
-195.17	38.478	-258.86	19.574

The effects on electrical resistance of pressure,¹ of tension,² and of a magnetic field³ have been investigated. The specific electrical resistance of a single crystal of bismuth is 1.38×10^{-4} ohm-cm. parallel to the trigonal axis, and 1.07×10^{-4} ohm-cm. perpendicular to that axis.⁴ At low temperatures the variation of electrical resistance of a single crystal with temperature⁵ is as follows (the value for the resistance is given as a ratio between the actual resistance at the temperature stated (R) and that at 0° C. (R_0)).

ELECTRICAL RESISTANCE OF SINGLE CRYSTALS OF BISMUTH AT LOW TEMPERATURES.

Parallel to Trigonal Axis.		Perpendicular to Trigonal Axis.	
Temperature, ° C.	$\frac{100R}{R_0}$	Temperature, ° C.	$\frac{100R}{R_0}$
-96.1	72.0	-92.1	66.3
-124.1	66.9	-128.1	57.1
-161.1	60.2	-149.1	50.5
		-157.1	47.2

The influence of a magnetic field upon the electrical resistance of a single crystal has been investigated⁶ at low temperatures.⁷

¹ Bridgman, *Proc. Nat. Acad. Sci.*, 1920, 6, 505.

² Zavattiero, *Atti R. Accad. Lincei*, 1920, 29, I, 48; Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1922, 57, 41; Rolnick, *Phys. Review*, 1930, 36, 506.

³ Corbino, *Atti R. Accad. Lincei*, 1920, 28, I, 49; McAlpine, *Phys. Review*, 1929, 33, 284; 1931, 37, 624; Altmann, *Sitzungsber. Naturforsch.-Ges. Univ. Tarka*, 1928, 35, 8; Becker and Curtis, *Phys. Review*, 1920, 15, 457. See also Carpini, *Atti R. Accad. Lincei*, 1904, [5], 13, II, 159; Grunmach and Weidert, *Physikal. Zeitsch.*, 1906, 7, 729; Dewar and Fleming, *Phil. Mag.*, 1895, 39, 619; Gross, *Zeitsch. Physik*, 1930, 64, 520.

⁴ Kapitza, *Proc. Roy. Soc.*, 1928, 119 A, 358, 387, 401; 1929, 123 A, 292, 342; Schneider, *Phys. Review*, 1928, 31, 251.

⁵ *International Critical Tables*, 1929, 6, 125.

⁶ Kapitza, *loc. cit.*

⁷ Shubnikov and de Haas, *Proc. Acad. Sci. Amsterdam*, 1930, 33, 130, 363, 433.

The *thermal electromotive force* of bismuth with respect to platinum¹ is given (in microvolts) by

$${}_B E_{Pt} = -61.95(t^2 - t^1) + 0.0251(t^2 - t^1)^2 + 0.000262(t^2 - t^1)^3$$

between 0° and 268° C. Values have also been obtained for couples with copper,² constantan³ and lead.⁴ The thermoelectric force between stressed and unstressed bismuth has been measured.⁵ Several investigators have drawn attention to a discontinuity in the thermoelectric power of bismuth at a temperature near the melting point. The effect of orientation on the thermal electromotive force of a single crystal of bismuth with reference to copper⁶ between 20° and 100° C. (expressed in microvolts) is as follows :

EFFECT OF ORIENTATION ON THERMAL E.M.F. OF SINGLE CRYSTALS OF BISMUTH WITH REFERENCE TO COPPER.

Angle between Basal Cleavage Plane and Direction of Current.	Thermal E.M.F.
0° 0'	-55 (t ² - t ¹) - 0.0312(t ² - t ¹) ²
5° 5'	-56.6(t ² - t ¹) - 0.025(t ² - t ¹) ²
10° 0'	-61.4(t ² - t ¹) - 0.10(t ² - t ¹) ²
17° 7'	-61.4(t ² - t ¹) - 0.0625(t ² - t ¹) ²
21° 1'	-61.1(t ² - t ¹) - 0.0875(t ² - t ¹) ²

Bismuth is diamagnetic. The *specific magnetic susceptibility*⁷ is -1.346×10^{-6} . The effect of temperature has been studied⁸ and the magnetic susceptibility of molten bismuth is found to be approximately one-hundredth that of solid bismuth just below the melting point.

¹ *International Critical Tables*, 1929, 6, 214. See also Pélabon, *Compt. rend.*, 1923, 176, 1305; *Ann. physique*, 1920, 13, 169; Wagner, *Ann. Physik*, 1908, [4], 27, 955; Jaeger and Diesselhorst, *Wissenschaftl. Abhandl. phys. tech. Reichsanst.*, 1900, 3, 269; Dewar and Fleming, *Phil. Mag.* 1895, [5], 40, 95.

² van Aubel, *Bull. Acad. roy. Belg.*, 1926, [5], 12, 559.

³ Boydston, *Phys. Review*, 1927, 30, 911.

⁴ *International Critical Tables*, loc. cit. See also Todesco, *Atti R. Accad. Lincei*, 1927, [6], 5, 434; *Nuovo Cim.*, 1927, 4, 94; Terada, Tanaka and Kysaba, *Proc. Imp. Acad. Tokyo*, 1927, 3, 132, 200; Bridgman, *Proc. Nat. Acad. Sci.*, 1925, 11, 608; Borelius and Lindh, *Ann. Physik*, 1917, 63, 97; Darling and Grace, *Proc. Phys. Soc. Lond.*, 1916, 29, 82; Koenigsberger, *Ann. Physik*, 1915, 47, 563; Jordan, *Phil. Mag.*, 1911, 21, 454; Caswell, *Phys. Review*, 1911, 33, 381; Lownds, *Ann. Physik*, 1901, 6, 146; Perrot, *Arch. Sci. phys. nat.*, 1898, 6, 105, 229, 899; 7, 149.

⁵ Wagner, loc. cit.

⁶ Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1918, 53, 269; 1926, 61, 101; 1929, 63, 351; *Phys. Review*, 1917, 9, 269; *Proc. Nat. Acad. Sci.*, 1928, 14, 943. See also *International Critical Tables*, loc. cit.; Boydston, loc. cit.; Terada, Tanaka and Kysaba, loc. cit.

⁷ Isnardi and Gans, *Ann. Physik*, 1920, [4], 61, 585. See also Endo, *Sci. Rep. Tohoku Imp. Univ.*, 1927, 16, 201; Ehrenfest, *Physica*, 1925, 5, 388; Onnes and Perrier, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 799; 1911, 13, 115; 1912, 14, 674; 1914, 16, 894, 901; Owen, *Ann. Physik*, 1912, 37, 657; Meslin, *Ann. Chim. Phys.*, 1906, [8], 7, 145; Wills, *Phil. Mag.*, 1896, [5], 45, 432; *Phys. Review*, 1905, 20, 188; Curie, *Compt. rend.*, 1892, 115, 1292; 1893, 116, 136; *J. Physique*, 1895, 4, 197; Lombardi, *Mem. R. Accad. Torino*, 1897, [2], 47, 1; Fleming and Dewar, *Proc. Roy. Soc.*, 1896, 60, 283; 1898, 63, 311; von Ettingshausen, *Wied. Annalen*, 1882, 17, 272.

⁸ Honda, *Ann. Physik*, 1910, [4], 32, 1027.

The susceptibility is independent of the field strength at ordinary temperatures, but at temperatures of -250°C . or -260°C . it decreases at higher field strengths.¹ It is also decreased by cold working.² The magnetic properties of colloidal bismuth have been investigated with a view to determining the effect of particle size.³ Although the results of these investigations do not appear to be conclusive, it is suggested that the high diamagnetism of bismuth is a property of the crystal rather than of the atom.⁴ The magnetic susceptibility of a single crystal of bismuth⁵ in a direction perpendicular to the principal crystallographic axis is $-(1.482 \pm 0.014) \times 10^{-6}$, and in a direction parallel to this axis $-(1.053 \pm 0.010) \times 10^{-6}$. The mean value is -1.340×10^{-6} . From this it may be deduced that the magnetic susceptibility of a polycrystalline aggregate is $-(1.340 \pm 0.013) \times 10^{-6}$. The effect of temperature⁶ and of field strength⁷ on the magnetic susceptibility of single crystals has been investigated.

The various galvanometric and thermomagnetic effects in bismuth, such as the *Hall effect*, the *Corbino effect*, the *Ettingshausen effect*, the *Nernst effect*, the *Righi-Leduc effect*, etc., have been studied at great length.⁸ The Hall effect is negative and increases in a negative direction as the magnetic field increases, apparently approaching a limiting value; the Hall coefficient decreases as the temperature rises, becoming zero at the melting point; the crystalline structure and the orientation of the principal crystallographic axis to the primary current and to the magnetic field greatly influence the magnitude of the Hall effect; it is probably for this reason that many published results are discordant. The Hall effect in a single crystal has also been investigated.⁹ The Nernst effect is positive.

It is known that a substance may be caused to emit electrons when it is illuminated by light of sufficiently high frequency; the longest wavelength capable of producing this effect is called the *photoelectric threshold*.¹⁰ The value for polycrystalline bismuth lies between λ 2980 Å and λ 3300 Å; that for a single crystal between λ 2804 Å and λ 2894 Å.

The *optical properties* of bismuth in the massive condition,¹¹ in the

¹ de Haas and van Alphen, *Proc. Acad. Sci. Amsterdam*, 1930, 33, 680; de Haas, *Nature*, 1931, 127, 335.

² Lowance and Constant, *Phys. Review*, 1931, 38, 1547.

³ Verma and Mathur, *J. Indian Chem. Soc.*, 1931, 6, 181; 1933, 10, 321; Rao, *Indian J. Physics*, 1931, 6, 241; 1932, 7, 35; *Nature*, 1931, 128, 153; Bhatnagar, *J. Indian Chem. Soc.*, 1930, 7, 957; Vaidyanathan, *Indian J. Physics*, 1930, 5, 559; *Nature*, 1930, 125, 672.

⁴ For further references to the magnetic properties of bismuth, see Goetz and Focke, *Science*, 1931, 74, 603; *Phys. Review*, 1931, 38, 1569; Ehrenfest, *Zeitsch. Physik*, 1929, 58, 719; Ramon, *Nature*, 1929, 124, 412; Gross, *Zeitsch. Physik*, 1928, 50, 740.

⁵ Goetz and Focke, *Phys. Review*, 1934, 45, 170; Focke, *Phys. Review*, 1930, 36, 319. See also Nusbaum, *Phys. Review*, 1927, [2], 29, 370, 905; Forrest, *Trans. Roy. Soc. Edin.*, 1927, 54, 601.

⁶ McLennan and Cohen, *Trans. Roy. Soc. Canada*, 1929, III, [3], 23, 159; Donat and Stierstadt, *Ann. Physik*, 1933, 17, 897.

⁷ Stierstadt, *Zeitsch. Physik*, 1933, 80, 636.

⁸ Campbell, "*Galvanometric and Thermomagnetic Effects*" (London, 1923) (with bibliography). See also *International Critical Tables*, 1929, 6, 414.

⁹ Heaps, *Phys. Review*, 1927, [2], 30, 61.

¹⁰ *International Critical Tables*, 1929, 6, 68. See also Hamer, *Rev. Sci. Instruments*, 1924, 9, 251; Parmley, *Phys. Review*, 1927, 29, 202; 30, 656; Hughes, *Phil. Trans.*, 1912, 312, 205; Richardson and Compton, *Phil. Mag.*, 1912, 24, 575; Scharf, *Zeitsch. Physik*, 1928, 49, 827.

¹¹ Mayer, *Ann. Physik*, 1910, 31, 1017; Hagen and Rubens, *ibid.*, 1900, 1, 352.

form of opaque films,¹ in the molten condition² and in the form of single crystals³ have been investigated.⁴

Spectrum.—Bismuth compounds impart no characteristic coloration to the Bunsen flame. The wavelengths of the principal lines in the *arc spectrum* are as follows.⁵ (The numbers in parenthesis indicate the relative intensities of the lines, the lowest numbers indicating the weakest intensities.⁶)

11711 (10),	9657.2 (10),	8210.8 (10),	6134.85 (5),	5742.55 (6),
5552.24 (8),	4722.7 (8),	4722.5 (10),	4722.2 (10),	4121.85 (6),
4121.52 (6),	3510.85 (6),	3397.21 (5),	3067.73 (9),	3024.64 (8),
2993.34 (9),	2989.04 (9),	2938.31 (10),	2897.98 (10),	2809.63 (8),
2780.52 (7),	2730.50 (5),	2696.76 (6),	2627.93 (8),	2524.52 (7),
2515.68 (6),	2489.4 (5),	2400.89 (8),	2276.57 (5),	2230.62 (8),
2228.25 (6),	2189.59 (6),	2177.3 (6),	2152.9 (7),	2134.4 (8),
2133.6 (7),	2110.3 (8),	2061.71 (8),	1533.7 (5),	

The wavelengths of the most persistent lines in the arc spectrum, such as may be used for spectrochemical purposes, are as follows. (The expressions in parenthesis are the spectral terms allotted to the particular lines, adopting the usual notation.)

2061.71 ($^4S_2 - ^4P_3$),	2276.57 ($^4S_2 - ^4P_2$),	2780.52 (2D_2),
2809.63 ($^2D_3 - ^2P_2$),	2897.98 ($^2D_2 - ^2P_1$),	2938.31 (2D_3),
2989.04 (2D_2),	3067.73 ($^4S_2 - ^4P_1$),	

The "*raie ultime*," or most persistent line,⁷ has the wavelength 3067.73 Å.

The wavelengths of the principal lines in the *spark spectrum* are as follows. (The numbers in parenthesis indicate the relative intensities of the lines.)

6309.1 (7),	6600.1 (7),	5209.28 (10),	5144.50 (6),	4722.7 (8),
4722.5 (8),	4722.2 (5),	4561.15 (8),	4302.13 (10),	4259.64 (10)
4079.22 (10),	3792.9 (8),	3695.53 (8),	3510.85 (5),	3067.73 (6),
2989.04 (5),	2938.3 (8),	2897.98 (5),	1346 (10),	1317 (15),
1306 (10),	1051 (10),	1045 (10),		

The second and third order spectra have also been investigated,⁸ and it is indicated that the spectrum of singly ionised bismuth is that of

¹ Hulburt, *Astrophys. J.*, 1915, 42, 205.

² Aster, *Phys. Review*, 1922, 20, 349.

³ Rouse, *Phys. Review*, 1926, 27, 247; Dix and Rouse, *J. Optical Soc. Amer.*, 1927, 14, 304.

⁴ For a discussion of the relationship between the physical properties and the structure of bismuth, see Jones, *Proc. Roy. Soc.*, 1934, 147 A, 404.

⁵ For tables of wavelengths and sensibilities for use in spectrum analysis, see Pina de Rubies and Bargues, *Zeitsch. anorg. Chem.*, 1933, 215, 205; Krämer, *Zeitsch. anal. Chem.*, 1934, 97, 89.

⁶ *International Critical Tables*, 1929, 5, 284.

⁷ *International Critical Tables*, 1929, 5, 323.

⁸ McLennan, McLay and Crawford, *Proc. Roy. Soc.*, 1930, 129 A, 579. See also Kishen, *Current Science*, 1933, 1, 312; Zumstein, *Phys. Review*, 1931, 38, 2214; Green and Wulff, *ibid.*, 1931, 38, 2186; Green, *ibid.*, 1931, 37, 1687; Fisher and Goudsmit, *ibid.*, 1931, 37, 51; Arvidson, *Nature*, 1930, 126, 565; Lang, *Phys. Review*, 1928, 32, 737; Rao and Narayan, *Proc. Fifteenth Indian Sci. Cong.*, 1928, 80.

the two-electron spectrum, and that of doubly ionised bismuth a simple one-electron doubled spectrum. The bismuth nucleus has a resultant moment of momentum¹

$$\frac{4\frac{1}{2}\hbar}{2\pi} \quad (h = \text{Planck's constant})$$

The *ionisation potential* for singly ionised bismuth is about 14 volts, that for doubly ionised bismuth 25.4 volts and that for Bi^{V} 55.7 volts.²

The arc³ and spark⁴ spectra in the ultra-violet region have been studied in some detail, and in the latter case the spectrum has been extended to a wavelength of λ 200 Å.⁵

The *Zeeman effect* has been studied.⁶

In the *absorption spectrum* of bismuth vapour both lines and bands are found, in addition to the "*raie ultime*" (λ 3067.73 Å.). The bands appear in groups, occurring in the ultra-violet, and at higher temperatures, in the visible region. Each group consists of bands degraded towards the red. The approximate wavelengths of the bands in the ultra-violet region are (in Å.) 2859.9, 2842.9, 2828.2, 2813.5, 2799.8, 2785.0, 2772.7, 2759.6, 2744.8, 2732.6, 2722.0, 2712.3, 2701.9, 2693.2, 2681.5, 2670.0. The lines 2276, 2230 and 2228 are also strongly absorbed, and there are other absorption lines of wavelength 2110, 2062 and 2021 Å. At 800° C. fine absorption lines appear in the spectrum, the wavelengths of which do not appear to have been determined, while another banded structure is revealed at a lower wavelength. At about 1200° C. a banded structure is observed in the visible region extending from λ 4500 to λ 6500 Å. The interval between the bands in this spectrum differs from about 35 Å. at the violet end to about 90 Å. at the red end. At higher temperatures the bands tend to merge into one continuous band.⁷

The following are the wavelengths of absorption lines which are

¹ Back and Goudsmit, *Zeitsch. Physik*, 1928, 47, 194.

² For the hyperfine structure of the spark spectra of bismuth, and deductions concerning the nuclear structure, see also Schoepfle, *Phys. Review*, 1935, 47, 232; McLay and Crawford, *Proc. Roy. Soc.*, 1934, 143 A, 540; *Phys. Review*, 1933, 44, 986; Mohammed and Sharma, *Phil. Mag.*, 1932, 14, 977, 1143; Bacher and Wulff, *Phys. Review*, 1932, 40, 123; McLennan, McLay and Crawford, *Proc. Roy. Soc.*, 1931, 133 A, 652; Zeeman, Back and Goudsmit, *Zeitsch. Physik*, 1930, 66, 1; Back and Wulff, *ibid.*, p. 10; White, *Phys. Review*, 1929, 34, 1404; Back and Goudsmit, *Phys. Review*, 1928, 31, 1125; Nagaoka and Mishima, *Proc. Imp. Acad. Japan*, 1926, 2, 249; Ruark and Chenault, *Phil. Mag.*, 1925, 50, 937; Joos, *Physikal. Zeitsch.*, 1925, 26, 380; Nagaoka and Sugura, *Astrophys. J.*, 1921, 53, 339; Darbyshire, *Phil. Mag.*, 1933, 16, 761.

³ McLennan, Young and Ireton, *Proc. Roy. Soc.*, 1921, 98 A, 101.

⁴ Arvidson, *Ann. Physik*, 1932, 12, 787; Mohammed and Sharma, *loc. cit.*; Zumstein, *loc. cit.*; Lang, *Phil. Trans.*, 1924, 224, 418; Bloch and Bloch, *Compt. rend.*, 1914, 158, 1416; 1920, 170, 320; 1920, 171, 709; 1924, 178, 472; *J. Phys. Radium*, 1921, 2, 229.

⁵ For the infra-red spectrum, see Walters, *Bureau of Standards Scientific Papers*, 1921, No. 411, 161; Lubovich and Pearen, *Proc. Trans. Roy. Soc. Canada*, 1922, [3], 16, 195.

⁶ Back and Goudsmit, *Phys. Review*, 1928, 31, 1125. For bibliography to 1927, see *International Critical Tables*, 1929, 5, 420.

⁷ Frayne and Smith, *Phil. Mag.*, 1926, [7], 1, 735; Rao, *Proc. Roy. Soc.*, 1925, 107 A, 760; Narayan and Rao, *Phil. Mag.*, 1925, [6], 50, 647; Williams, *Physikal. Zeitsch.*, 1932, 33, 152; Barratt and Bonar, *Phil. Mag.*, 1930, [7], 9, 519; Charola, *Univ. la Plata, Estudio Ciencias*, 1929, 89, 205; *Physikal. Zeitsch.*, 1930, 31, 457; Zumstein, *Phys. Review*, 1926, 27, 562; Ruark, Mohler, Foote and Chenault, *U.S. Bureau of Standards Scientific Papers*, 1924, No. 490, 463; *Nature*, 1923, 112, 831; Grotrian, *Zeitsch. Physik*, 1923, 18, 169.

observed in the under-water spark spectrum; they correspond with those which are reversed in the arc spectrum: ¹

3596·11, 3510·85, 3405·23, 3397·21, 3067·73, 3024·64, 2993·34,
2989·04, 2938·31, 2897·98, 2809·63, 2780·52, 2730·5, 2696·76,
2627·93, 2524·52, 2515·68, 2400·89, 2276·57, 2230·62, 2228·25,
2189·59, 2177·3, 2164·1, 2156·9, 2153·5, 2152·9, 2134·4,
2133·6, 2110·3, 2061·71.

At 1500° to 1600° C. bismuth vapour emits fluorescent radiation orange-yellow in colour.² The *fluorescence spectrum* shows a banded structure which is more or less the exact complement of the absorption spectrum in the region examined. The wavelengths of bands that have been measured are:

6533·0, 6464·5, 6389·0, 6319·5, 6248·5, 6187·5, 6117·5, 6052·0,
5991·5, 5940·5, 5886·5, 5831·5, 5776·5, 5726·0, 5680·0, 5640·0.

It is convenient here to include a description of the *spark spectrum* of *dilute solutions of bismuth trichloride*. The wavelengths of the most persistent lines in this spectrum, and the minimum concentration of the solution in the spectrum of which they appear, are given on p. 143. These lines may be employed in quantitative analysis.³

The *X-ray spectrum* of bismuth has been studied, and measurements obtained for the K,⁴ L,⁵ M⁶ and N⁷ series.

Chemical Properties of Bismuth.

Bismuth is not readily attacked by air at ordinary temperatures, but on heating in air it is converted to trioxide.⁸ When heated in air to its boiling point it burns with a faint bluish-white flame, forming bismuth trioxide, which condenses as a yellow deposit of "flowers of bismuth" (*flores bismuti*) upon a cold surface placed in the flame. It reacts slowly at ordinary temperatures with water from which carbon dioxide has been expelled, becoming coated with an hydrated oxide;⁹ and at red heat there is some evidence to indicate that it decomposes steam slowly.¹⁰

Bismuth is not attacked by hydrochloric acid in the absence of air,

¹ Hulburt, *Phys. Review*, 1924, 24, 129.

² Rao, *loc. cit.* See also McLennan, Walerstein and Smith, *Phil. Mag.*, 1927, [7], 3, 390; Terenin, *Zeitsch. Physik*, 1925, 31, 26; Narayan and Rao, *Nature*, 1924, 114, 646; Franck, *Physikal. Zeitsch.*, 1923, 24, 450.

³ Hartley, *Phil. Trans.*, 1884, 175, 327; Baly, "*Spectroscopy*" (London, 1927), 2, 144.

⁴ Stephenson and Cork, *Phys. Review*, 1926, 27, 138; Réchou, *Compt. rend.*, 1925, 180, 1107; Duane, Fricke and Stenström, *Proc. Nat. Acad. Sci.*, 1920, 6, 607.

⁵ Siegbahn and Friman, *Physikal. Zeitsch.*, 1916, 17, 17; Coster, *Zeitsch. Physik*, 1921, 4, 178; Friman, *ibid.*, 1926, 39, 813; Eddy and Turner, *Proc. Roy. Soc.*, 1927, 114 A, 605; Williams, *Phys. Review*, 1934, 45, 71; Duane and Patterson, *Proc. Nat. Acad. Sci.*, 1920, 6, 518.

⁶ Hjalmar, *Compt. rend.*, 1922, 175, 878; *Zeitsch. Physik*, 1923, 15, 65.

⁷ Dolejssek, *Zeitsch. Physik*, 1924, 21, 111; Hjalmar, *ibid.*, 1923, 15, 65. For further literature dealing with the X-ray spectrum, see also Robinson, *Proc. Roy. Soc.*, 1923, 104 A, 455; Allen, *Phys. Review*, 1924, 24, 1; Robinson and Cassie, *Proc. Roy. Soc.*, 1926, 113 A, 282; Kimura and Nakamura, *Japan. J. Physics*, 1924, 3, 29; Duane and Patterson, *Proc. Nat. Acad. Sci.*, 1922, 8, 85; *International Critical Tables*, 1929, 6, 70.

⁸ Thomson, *Proc. Phil. Soc. Glasgow*, 1841-2, 1, 4; Heintz, *Pogg. Annalen*, 1844, 63, 58.

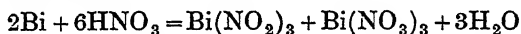
⁹ von Bonsdorff, *Pogg. Annalen*, 1837, 41, 305.

¹⁰ Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 363.

SPARK SPECTRUM OF DILUTE SOLUTIONS OF BISMUTH TRICHLORIDE.

1 per cent. Solution.	0.1 per cent. Solution.	0.01 per cent. Solution.
3792.9
3695.5
3595.7
3510.8
3430.9
3396.7
3067.7	3067.7	3067.7
3023.8	3023.8	..
2992.2	2992.2	..
2989.0
2938.3
2897.9	2897.9	..
2854.8	2854.8	..
2846.1	2846.1	..
2414.8

but in the presence of air it is slowly dissolved. No hydrogen is evolved. It is readily dissolved by cold nitric acid or aqua regia and by hot concentrated sulphuric acid; it is possible that the solvent action of nitric acid is due to the presence of nitrous acid.¹ The nitrous acid is presumed to act catalytically, and the reaction may possibly be represented by the equation



In the presence of nitric acid, any bismuth nitrite formed is at once converted to bismuth nitrate with the production of oxides of nitrogen. Bismuth thus resembles silver, mercury and copper in this reaction. With nitric acid of density 1.2, and at a temperature of 65° C., bismuth reacts with instantaneous evolution of nitrogen tetroxide (even in an atmosphere of hydrogen), and evolution of this gas continues until all the metal is dissolved. Neither ammonia nor hydroxylamine is produced by the action of nitric acid on bismuth under any conditions. Bismuth does not react with phosphoric acid, either in dilute or concentrated solution.² It is oxidised slowly by chloric acid and the product is only partially soluble³ in water.

Metallic bismuth does not react with hydrogen even when heated. A black powder, described as pyrophoric bismuth, can be prepared by the reduction of bismuth compounds with hydrogen.⁴ From solutions of its compounds, bismuth may be displaced by hydrogen under pressure. From solutions of bismuth trichloride up to normal concentration, and with pressures between 15 and 250 atmospheres and temperatures

¹ Stansbie, *J. Soc. Chem. Ind.*, 1908, 27, 365; Divers, *ibid.*, 1904, 23, 1182; *J. Chem. Soc.*, 1885, 47, 230; 1883, 43, 443. See also this Series, Vol. VI, Part I, p. 198.

² Portevin and Sanfourche, *Compt. rend.*, 1931, 192, 1563.

³ Hendrixson, *J. Amer. Chem. Soc.*, 1904, 26, 747.

⁴ Vanino and Menzel, *Zeitsch. anorg. Chem.*, 1925, 149, 18.

between 150° and 200° C., this displacement may be represented by the expression

$$\frac{1}{\theta p} \log \frac{a}{a-x} = K$$

From this it is calculated that from a normal solution of bismuth trichloride at 20° C. and with hydrogen at 100 atmospheres pressure, one per cent. of bismuth would be precipitated in thirty-seven years. There are reasons for believing that the reaction is ionic. Precipitation of bismuth from acetic acid solutions takes place more rapidly than from solutions in hydrochloric acid. Hydrogen under a pressure of 60 atmospheres will also displace bismuth from the triphenyl derivative dissolved in xylene, according to the equation



At 225° C. this reaction is complete.¹

Bismuth does not react readily with the halogens when the latter are perfectly dry; the presence of moisture, however, greatly accelerates reaction. The metal is attacked only superficially by fluorine even at red heat; it reacts with chlorine, bromine and iodine to form in each case an impure halide, which may possibly be a mixture of the di-halide with the tri-halide.²

Bismuth is oxidised by ozone, the product being a mixture of oxides.³

The metal combines directly with sulphur, selenium and tellurium when melted with those elements. It combines with sulphur when a mixture of the two elements is submitted to pressure.⁴ It does not react with dry sulphur dioxide even on heating, but when heated with sulphurous acid under pressure bismuth trisulphide is formed.⁵

Bismuth does not combine directly with nitrogen, and with phosphorus only with difficulty. With arsenic and antimony it forms alloys; it is doubtful if intermetallic compounds are formed with either (see, however, p. 214). It is oxidised to trioxide by the action of nitric oxide⁶ at 200° C. It is very slowly attacked by ammonium nitrate.⁷

Bismuth will dissolve to a slight extent in solutions of alkalis, and evidence has been obtained of the formation of alkali bismuthites.⁸

The position of bismuth in the *electromotive series* is a little doubtful; in the series as usually given its position is anomalous, since it lies between antimony and arsenic, thus :

¹ Ipatiev, Jun., *Ber.*, 1931, 64 B, 2725; Ipatiev, Jun., Molentin and Teodorovich, *Ber.*, 1931, 64 B, 1964; Ipatiev and Razuvaev, *Ber.*, 1930, 63, 1110. For the action of the free radicals methyl and ethyl on bismuth, see Paneth, *Trans. Faraday Soc.*, 1934, 30, 179.

² Thomas and Dupais, *Compt. rend.*, 1906, 143, 282; Cowper, *J. Chem. Soc.*, 1883, 43, 153; *Chem. News*, 1883, 47, 70; Thomsen, *Ber.*, 1883, 16, 40; Muir, *J. Chem. Soc.*, 1876, 29, 144; Déherain, *Bull. Soc. chim.*, 1862, 4, 22; Weber, *Pogg. Annalen*, 1859, 107, 598; Schneider, *ibid.*, 1855, 96, 130; Heintz, *ibid.*, 1844, 63, 60; Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 247.

³ Schönbein, *J. prakt. Chem.*, 1864, 93, 59.

⁴ Spring, *Ber.*, 1883, 16, 1001.

⁵ Geitner, *Annalen*, 1864, 129, 354; Uhl, *Ber.*, 1890, 23, 2154; Schiff, *Annalen*, 1861, 117, 95.

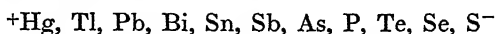
⁶ Muller and Barck, *Zeitsch. anorg. Chem.*, 1923, 129, 309.

⁷ Tammann, *ibid.*, 1922, 121, 275.

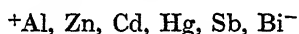
⁸ Grube and Schweigardt, *Zeitsch. Elektrochem.*, 1923, 29, 257.

Cs . . . Zn, Cd, Fe, Co, Ni, Sn, Pb, H, Sb, Bi, As, Cu, Hg, Ag,
Pd, Pt, Au . . . F

If the elements are arranged in the order of the heats of formation of the chlorides the following series is obtained :—



which is in fair agreement with the order of the electrode potentials. All the elements in this series are electronegative to elements which are truly electropositive, such as the alkali metals, and are electropositive to those which are truly electronegative, such as the halogen elements. They may be regarded as amphoteric, a view that is supported by the behaviour of their compounds with alkali metals.¹ Many of these compounds are metallic in character, and are decomposed by water, probably hydrolytically, with the formation of a hydride of the more electronegative element. (Evidence for this has been obtained in the case of sodium stannide.) These compounds with alkali metals are, however, soluble without decomposition in liquid ammonia, and the solutions behave as electrolytic conductors. Thus in a solution of sodium bismuthide in liquid ammonia it is probable that the anion is composed of a group of bismuth atoms, sodium forming the cation, since these solutions behave similarly to those of ordinary salts, and show no metallic properties. The electromotive series for these amphoteric elements corresponds with the series given above derived from the heats of formation of their chlorides, although the position of bismuth and phosphorus is doubtful owing to the sluggish action of their alkali compounds in solution in liquid ammonia.² From the decomposition voltages of metallic bromides dissolved in aluminium bromide the electromotive series is found to be ³



In the electrolysis of fused alloys of copper, tin and bismuth at 1000° C. copper migrates to the cathode and tin and bismuth to the anode.⁴

Bismuth can be precipitated from solution completely by tin, zinc, cadmium, iron, manganese and magnesium,⁵ but only partially by lead and copper.⁶

The *electrode potential* of bismuth has been determined with respect to various cells. The normal potential between bismuth and a normal solution of a bismuth salt in the cell ⁷



is, for bismuth sulphate -0.490 volt, for bismuth chloride -0.315 volt and for bismuth nitrate -0.500 volt. By calculation from the hydrogen-bismuth cell, using hydrochloric acid, the specific potential ⁸ is -0.1635

¹ Kraus, *Trans. Amer. Electrochem. Soc.*, 1924, 45, 175.

² Bergstrom, *J. Amer. Chem. Soc.*, 1925, 47, 1503. For the relationship of bismuth to the radioactive elements, see Joliot, *J. Chim. phys.*, 1930, 27, 119.

³ Isbekow, *Zeitsch. physikal. Chem.*, 1925, 116, 304. See also Isbekow, *Zeitsch. anorg. Chem.*, 1930, 185, 324.

⁴ Kremann and Scheibel, *Monatsh.*, 1931, 57, 241.

⁵ Prelinger, *Monatsh.*, 1893, 14, 369; Faktor, *Pharm. Post*, 1905, 38, 153. See also Kroll, *Metall und Erz*, 1922, 19, 317.

⁶ Jacquelin, *J. prakt. Chem.*, 1838, 14, 1; Reinsch, *ibid.*, 1841, 24, 248.

⁷ Neumann, *Zeitsch. physikal. Chem.*, 1894, 14, 193.

⁸ Noyes and Chow, *J. Amer. Chem. Soc.*, 1918, 40, 739. See also Jellinek and Kühn, *Zeitsch. physikal. Chem.*, 1923, 105, 337.

volt at 15° C., -0.1599 volt at 25° C. and -0.1563 volt at 35° C. In molar solutions of bismuth perchlorate the bismuth may be present either as BiO^+ or as BiOH^{++} . The electrode potential has been calculated from e.m.f. measurements upon such solutions using a bismuth electrode.¹ Assuming that all the bismuth is present as BiO^+ the potential is -0.814 volt; assuming that it is all present as BiOH^{++} the potential is -0.298 volt.

Smooth crystalline cathode deposits of bismuth can be obtained by electrolysis of a solution of bismuth perchlorate.² The recommended solution contains 4 grams of bismuth trioxide and 10.4 grams of perchloric acid in 100 c.c. of solution, with, as addition reagents, 0.03 per cent. of glue and 0.08 per cent. of cresol. In the absence of addition reagents, the decomposition voltage of bismuth perchlorate is 1.62 volts; for deposition a current density of 3.1 amperes per square decimetre is recommended. At present there appears to be very little practical demand for electro-deposited bismuth, but it is possible that the process may be applicable to the manufacture of certain components for electrical and magnetic apparatus.³ The process does not appear to be suitable for the refining of bismuth.

In a normal solution of bismuth silicofluoride⁴ the electrode potential, compared with the hydrogen electrode, is -0.295 volt. It is reported that a Japanese company employs a solution of this nature for the refining of bismuth.⁵

The overvoltage for bismuth⁶ in 2N H_2SO_4 at 25° C. is 0.388 ± 0.004 volt.

The anodic corrosion of bismuth in nitrate solutions has been studied;⁷ under suitable conditions bismuthyl nitrate is formed. In alkaline solutions bismuth dissolves anodically to form alkali bismuthite. When the concentration of the solution exceeds one gram of bismuth per litre the anode becomes passive as a result of the formation of a coating of oxides of bismuth.⁸ Bismuth also dissolves at the cathode in alkaline solution.⁹

Sols of bismuth have been prepared in a variety of ways. In the earlier methods, organic salts of bismuth were reduced in very dilute solution, as for the preparation of bismuth monoxide.¹⁰ The electric pulverisation method has also been employed.¹¹ More recently, investigators have employed chiefly reduction methods, formaldehyde, sodium bisulphite and sodium thiosulphate being used as reducing agents. The sols produced are frequently very unstable, but the stability is greatly increased by the addition of protective colloids.

¹ Smith, *J. Amer. Chem. Soc.*, 1923, 45, 360; Swift, *ibid.*, p. 371.

² Harbaugh and Mathers, *Trans. Amer. Electrochem. Soc.*, 1933, 64, 293.

³ See further, Fink and Gray, *ibid.*, 1932, 62, 123.

⁴ Förster and Schwabe, *Zeitsch. Elektrochem.*, 1910, 16, 279.

⁵ *Eng. Mining J.*, 1929, 128, 89.

⁶ Thiel and Hamerschmidt, *Zeitsch. anorg. Chem.*, 1923, 132, 15. See also Lloyd, *Trans. Faraday Soc.*, 1929, 25, 525.

⁷ Prideaux and Hewis, *J. Soc. Chem. Ind.*, 1922, 41, 176.

⁸ Grube and Schweigardt, *Zeitsch. Elektrochem.*, 1923, 29, 257. See also Newberry, *J. Chem. Soc.*, 1916, 109, 1066.

⁹ Paneth, *Zeitsch. Elektrochem.*, 1925, 31, 572.

¹⁰ Vanino and Treubert, *Ber.*, 1899, 32, 1072; Vanino, *Pharm. Zentr.-h.*, 1899, 40, 276; Lottermoser, *J. prakt. Chem.*, 1899, 59, 489; Gutbier and Hofmeier, *Zeitsch. anorg. Chem.*, 1905, 44, 225.

¹¹ Bredig, *Zeitsch. Elektrochem.*, 1897, 4, 514; *Zeitsch. angew. Chem.*, 1898, 11, 951; Bredig and Haber, *Ber.*, 1898, 31, 2741; Svedberg, *Ber.*, 1905, 38, 3616; 1906, 39, 1705.

There is evidence that many of these sols are contaminated by oxide.¹ Evidence of sol formation has been observed during electrolysis of distilled water between bismuth electrodes using a low voltage.²

Atomic Weight of Bismuth.

[Note.—The bracketed numbers refer to list of references under table on p. 148.]

Until comparatively recent years the values obtained for the atomic weight of bismuth by different investigators varied considerably. This was, in general, due to two causes: firstly, the difficulty of obtaining pure bismuth compounds, and secondly, the tendency for inorganic salts of bismuth to form basic complexes through hydrolysis. The earliest values were obtained by Lagerhjelm,⁽¹⁾ who converted metallic bismuth into oxide, sulphide and sulphate respectively and determined the ratios $2\text{Bi} : \text{Bi}_2\text{O}_3$, $2\text{Bi} : \text{Bi}_2\text{S}_3$, and $2\text{Bi} : \text{Bi}_2(\text{SO}_4)_3$. Subsequently many investigators repeated these determinations and obtained values varying from 208 to 210. Dumas⁽³⁾ converted the metal into chloride and determined the ratio $3\text{Ag} : \text{BiCl}_3$. Marignac⁽⁴⁾ prepared bismuth trioxide from bismuth nitrate. The nitrate was first purified and then converted into basic nitrate, the latter being converted into the oxide by heating. In one series he reduced the oxide to metal by heating in a current of hydrogen and determined the ratio $2\text{Bi} : \text{Bi}_2\text{O}_3$; in another he converted the oxide into the sulphate and determined the ratio $\text{Bi}_2\text{O}_3 : \text{Bi}_2(\text{SO}_4)_3$. Classen,⁽⁶⁾ in 1890, realising the difficulty of obtaining pure bismuth, purified the metal electrolytically; from the ratio $2\text{Bi} : \text{Bi}_2\text{O}_3$ he obtained the value 208.92, which approximates closely to that now generally accepted. Later, Gutbier^{(8), (9), (10)} and his collaborators adopted a variety of methods and obtained values all of which were in the neighbourhood of 208. More recently, Hönigschmid and Birckenbach⁽¹³⁾ prepared specimens of the chloride and bromide of bismuth with great care, taking special precautions to exclude all moisture, and from their analyses of these salts obtained a mean value of 209. Classen^{(12), (14)} and his collaborators concluded that organic compounds of bismuth would be more suitable for atomic weight determinations as they were less liable to form basic complexes. They prepared specimens of bismuth triphenyl, and from the ratio $2\text{BiPh}_3 : \text{Bi}_2\text{O}_3$ derived the mean value 209.00. The chief values obtained by different investigators are recorded in the table on p. 148.

In 1921 the value adopted by the International Committee was 208.00; at present (1936) the accepted value is 209.00. This is in agreement with the work of Aston,³ who determined the mass number of bismuth to be 209.

Bismuth is a simple element, no inactive isotopes having been discovered.⁴ Radioactive isotopes, such as thorium C, are known, however.

¹ Gutbier, Ottenstein and Adam, *Zeitsch. anorg. Chem.*, 1927, 164, 287; Gutbier, *ibid.*, 1926, 151, 153; Gutbier, Kautter and Getner, *ibid.*, 1925, 149, 187; Gutbier and Kautter, *ibid.*, 1925, 146, 166; Lapenta and Reisler, *U.S. Patent*, 1927, 1615226; Paal and di Pol, *Ber.*, 1926, 59 B, 877; Hugounenq and Loiseleur, *Compt. rend.*, 1926, 182, 851.

² Pavlov, *Kolloid Zeitsch.*, 1924, 34, 100. See also Moriguchi, *J. Chem. Soc. Japan*, 1933, 54, 1047.

³ Aston, *Nature*, 1924, 114, 717; *Phil. Mag.*, 1925, 49, 1191.

⁴ Aston, *loc. cit.* See, however, Allison and Bishop, *Phys. Review*, 1933, 43, 48; Chemisches Werk Klopfer, G.M.B.H., *German Patent*, 1930, 540983.

THE ATOMIC WEIGHT OF BISMUTH.

Authority.	Ratio Determined.	No. of Expts.	Atomic Weight.
Lagerhjelm ⁽¹⁾ (1814)	2Bi : Bi ₂ S ₃ = 100 : 122.32	4	215
	2Bi : Bi ₂ O ₃ = 100 : 111.3285	2	211.8
Schneider ⁽²⁾ (1851)	2Bi : Bi ₂ O ₃ = 89.6552 : 100	8	208.00
Dumas ⁽³⁾ (1859)	3Ag : BiCl ₃ = 100 : 98.008	9	210.806
Marignac ⁽⁴⁾ (1883)	2Bi : Bi ₂ O ₃ = 89.682 : 100	6	208.60
	Bi ₂ O ₃ : Bi ₂ (SO ₄) ₃ = 100 : 151.726	6	208.18
Löwe ⁽⁵⁾ (1883)	2Bi : Bi ₂ O ₃ = 89.648 : 100	2	207.84
Classen ⁽⁶⁾ (1890)	2Bi : Bi ₂ O ₃ = 89.696 : 100	9	208.92
Schneider ⁽⁷⁾ (1894)	2Bi : Bi ₂ O ₃ = 89.657 : 100	6	208.04
Gutbier and Birckenbach ⁽⁸⁾ (1908)	2Bi : Bi ₂ O ₃ = 89.656 : 100	10	208.02
	= 89.662 : 100	6	208.15
Gutbier and Mehler ⁽⁹⁾ (1908)	BiBr ₃ : 3AgBr = 79.467 : 100	8	207.959
Gutbier and Janssen ⁽¹⁰⁾ (1908)	2Bi : Bi ₂ (SO ₄) ₃ = 59.084 : 100	6	208.081
de Coninck and Gérard ⁽¹¹⁾ (1916)	BiCl ₃ : Bi = 2.1400 : 1.4165	4	208.40
Classen and Ney ⁽¹²⁾ (1920)	2BiPh ₃ : Bi ₂ O ₃ = 188.954 : 100	10	208.949
Hönigschmid and Birckenbach ⁽¹³⁾ (1921)	BiCl ₃ : 3AgCl = 73.3426 : 100	20	209.01
	= 73.3399 : 100	15	209.00
	BiBr ₃ : 3AgBr = 79.6474 : 100	14	208.98
	BiBr ₃ : 3Ag = 138.655 : 100	10	209.00
Classen and Strauch ⁽¹⁴⁾ (1924)	2BiPh ₃ : Bi ₂ O ₃ = 188.902 : 100	15	209.029

⁽¹⁾ Lagerhjelm, *Annals of Philosophy*, 1814, 4, 358.

⁽²⁾ Schneider, *Pogg. Annalen*, 1851, 82, 303.

⁽³⁾ Dumas, *Ann. Chim. Phys.*, 1859, 55, 176.

⁽⁴⁾ Marignac, *Arch. Sci. phys. nat.*, 1883, [3], 10, 10. See Bailey, *J. Chem. Soc.*, 1887, 51, 676.

⁽⁵⁾ Löwe, *Zeitsch. anal. Chem.*, 1883, 22, 498.

⁽⁶⁾ Classen, *Ber.*, 1890, 23, 938.

⁽⁷⁾ Schneider, *J. prakt. Chem.*, 1894, 50, 461.

⁽⁸⁾ Gutbier and Birckenbach, *ibid.*, 1908, 77, 457.

⁽⁹⁾ Gutbier and Mehler, *ibid.*, 1908, 78, 409.

⁽¹⁰⁾ Gutbier and Janssen, *ibid.*, 1908, 78, 421.

⁽¹¹⁾ de Coninck and Gérard, *Compt. rend.*, 1916, 162, 252.

⁽¹²⁾ Classen and Ney, *Ber.*, 1920, 53 B, 2267; *Zeitsch. anorg. Chem.*, 1921, 115, 253.

⁽¹³⁾ Hönigschmid and Birckenbach, *Ber.*, 1921, 54 B, 1873. See also Hönigschmid, *Zeitsch. Elektrochem.*, 1920, 26, 403.

⁽¹⁴⁾ Classen and Strauch, *Zeitsch. anorg. Chem.*, 1924, 141, 82.

Alloys of Bismuth.

Alloys of bismuth are not used to a great extent in industry. The low melting point of the metal, and the fact that it forms simple eutectiferous series of alloys with certain other metals, enables it to be used, however, in the manufacture of "fusible alloys."¹ These are mainly ternary or quaternary alloys of bismuth, tin, lead and cadmium; some typical analyses are as follows:

COMPOSITIONS OF SOME "FUSIBLE ALLOYS."

Name.	Bi.	Pb.	Sn.	Cd.	M.pt. (° C.).
Newton's . .	50	31	19	..	95
Rose's . .	50	28	22	..	100
Darcet's . .	50	25	25	..	98
Wood's . .	50	24	14	12	71
Lipowitz' .	50	27	18	10	M.pt. 70° C., softens at 60° C.

The freezing point diagrams, and in some cases the conditions of equilibrium, of a number of binary alloys of bismuth have been investigated. They may be described briefly as follows: ²

Bismuth-Lithium.³—Two compounds are formed: Li_3Bi (M.pt. 1145° C.) and LiBi (formed by a peritectic reaction at 415° C.). The latter is dimorphous, with a transition point at 400° C. No ranges of solid solution have been observed. There are two eutectics, at 14 atoms per cent. lithium (M.pt. 243° C.), between Bi and α LiBi , and at 97.5 atoms per cent. lithium (M.pt. 175° C.), between Li and Li_3Bi . Primary crystals of β LiBi are formed only between 35 and 37 atoms per cent. lithium.

Bismuth-Sodium.⁴—Two intermetallic compounds are indicated: Na_3Bi (M.pt. 790° C.) and NaBi (decomposing at 450° C.). A eutectic is formed at 97.5 per cent. bismuth (M.pt. 218° C.). The compound NaBi crystallises with a tetragonal, body-centred lattice: $a = 3.46 \text{ \AA}$, $c = 4.80 \text{ \AA}$. The unit cell contains one atom of each element, the lattice containing no complexes of bismuth atoms. Complexes, such as $\text{Na}_3\text{Bi}_5 \cdot x\text{NH}_3$, are however formed with liquid ammonia, which, on removal of ammonia, yield mixtures of NaBi and bismuth.⁵

Bismuth-Potassium.⁶—Two compounds are formed: KBi_2 (M.pt. 553° C.) and K_3Bi_2 (M.pt. 673° C.). A transformation occurs in the latter at 281° C. A eutectic is formed at the bismuth end of the system, melting at 64° C., and the liquidus curve shows discontinuities at 18 per

¹ Thews, *Metallbörse*, 1930, 20, 1097, 1153, 1211; Bureau of Standards, 1930, Circular No. 388; Parravano and Sirovich, *Gazzetta*, 1912, 42 I, 630; Hommel, *Zeitsch. Metallkunde*, 1921, 13, 456, 511, 565.

² *International Critical Tables*, 1927, 2, 419.

³ Grube, Vosskühler and Schlecht, *Zeitsch. Elektrochem.*, 1934, 40, 270.

⁴ Mathewson, *Zeitsch. anorg. Chem.*, 1906, 50, 171.

⁵ Zintl and Dullenkopf, *Zeitsch. physikal. Chem.*, 1932, B 16, 183.

⁶ Smith, *Zeitsch. anorg. Chem.*, 1908, 56, 109.

cent. bismuth (373° C.), 24 per cent. bismuth (423° C.) and 79 per cent. bismuth (281° C.). The compound KBi_2 crystallises with a cubic, face-centred lattice: $a = 0.501 \pm 0.005$ A. There are eight molecules in the unit cell.¹

Bismuth-Copper.²—These metals form a simple eutectiferous series of alloys with the eutectic close to the bismuth end, melting at 268° C. X-ray analysis reveals that the lattice of each metal remains unchanged and indicates that the mutual solubility is very low. The influence of bismuth on the mechanical properties of copper is considerable, the presence of 0.05 per cent. producing brittleness. The addition of arsenic mitigates to some extent the effect of bismuth. With more than 0.005 per cent. bismuth, copper is unsuitable for wire drawing.³

Bismuth-Silver.⁴—No compounds are formed. A eutectic is found at 2.5 per cent. silver (melting at 260° C.), and the maximum solid solubility of bismuth in silver is about 5.5 per cent. These results are confirmed by X-ray analysis.

Bismuth-Gold.⁵—A eutectic is formed at 83 per cent. bismuth (240° C.); the solid solubility of bismuth in gold is approximately 4.5 per cent. Although neither bismuth nor gold exhibits the phenomenon of superconductivity, the eutectic mixture becomes superconducting at -271.1° to -271.6° C. It is stated that the superconductivity is localised in the solid solution phase.⁶

Bismuth-Magnesium.⁷—One compound is formed, Mg_3Bi_2 (M.pt. 823° C.), which exists in two modifications, α and β , the transition temperature being 700° C. for the pure compound and slightly lower for alloys containing a slight excess of magnesium. There appears to be a slight range of solid solution of magnesium in the compound. Two eutectics are formed, at 14.3 atoms per cent. bismuth (M.pt. 551° C.) and at 95.7 atoms per cent. bismuth (M.pt. 260° C.).

Bismuth-Calcium.⁸—Two compounds are formed: CaBi_3 (decomposing at 506° C.) and Ca_3Bi_2 (M.pt. 928° C.). A third compound, CaBi , may also exist. There are two eutectics, at 0.5 per cent. calcium (M.pt. 270° C.) and at 88 per cent. calcium (M.pt. 785° C.). The heat of formation of the compound Ca_3Bi_2 at 21.5° C. is 51,600 gram-calories per mole.

Bismuth-Zinc.⁹—A eutectic is formed at 97 per cent. bismuth (M.pt. 250° C.). Within the range of composition between 1 and 70

¹ Zintl and Harder, *Zeitsch. physikal. Chem.*, 1932, B 16, 206.

² Jeriomin, *Zeitsch. anorg. Chem.*, 1907, 55, 412; Ehret and Fine, *Phil. Mag.*, 1930, [7], 10, 551.

³ Freude, *Metallbörse*, 1928, 18, 818; Johnson, *J. Inst. Metals*, 1912, 7, 240.

⁴ Petrenko, *Zeitsch. anorg. Chem.*, 1906, 50, 133; Broderick and Ehret, *J. Phys. Chem.*, 1931, 35, 2627, 3322.

⁵ Vogel, *Zeitsch. anorg. Chem.*, 1906, 50, 145.

⁶ de Haas and Jurriaanse, *Proc. Acad. Sci. Amsterdam*, 1932, 35, 748; *Naturwissenschaften*, 1931, 19, 706; de Haas, *Metallwirtschaft*, 1930, 9, 149; *Naturwissenschaften*, 1929, 17, 85; de Haas, van Aubel and Voogd, *Proc. Acad. Sci. Amsterdam*, 1929, 32, 226, 724.

⁷ Grube, Mohr and Bornhak, *Zeitsch. Elektrochem.*, 1934, 40, 143; Kawakami, *Sci. Rep. Tohoku Imp. Univ.*, 1930, 19, 521; Grube, *Zeitsch. anorg. Chem.*, 1906, 49, 72.

⁸ Kurzyniec, *Bull. Acad. polonaise*, 1931 A, 31. See also Donski, *Zeitsch. anorg. Chem.*, 1908, 57, 185; Kreman, Wastall and Schopper, *Forschungsarbeiten zur Metallkunde*, 1922, [5]; *J. Inst. Metals*, 1924, 32, 529.

⁹ Curry, *J. Phys. Chem.*, 1909, 13, 589; Honda and Ishigaki, *Sci. Rep. Tohoku Imp. Univ.*, 1925, 14, 219; Mathewson and Scott, *Zeitsch. Metallkunde*, 1914, 5, 1.

per cent. bismuth the melt, above 417° C., consists of two immiscible liquids.

Bismuth-Cadmium.¹—These metals form a simple eutectiferous system with a eutectic at 40 per cent. cadmium (M.pt. 149° C.).

Bismuth-Mercury.²—The two metals are mutually insoluble in the solid state; a eutectic is formed very close to the mercury end of the series (M.pt. -39° C.).

Bismuth-Aluminium.³—Within the range of composition between 3 and 98.7 per cent. bismuth the melt, above 650° C., consists of two immiscible liquids. The addition of small amounts of bismuth to aluminium causes a slight depression of the melting point, the maximum depression being 3.5° C. Bismuth is slightly soluble in aluminium in the solid state, but aluminium appears to be insoluble in bismuth.

Bismuth-Gallium.⁴—In this system there is a range of composition within which the melt consists of two immiscible liquids. The maximum solid solubility of gallium in bismuth is 11 per cent.

Bismuth-Thallium.⁵—In this system maxima occur on the liquidus curve at 10 per cent. bismuth (307° C.) and at 62 per cent. bismuth (220° C.); the latter corresponds to the compound Tl_3Bi_5 . Eutectics are found at 5 per cent. bismuth (M.pt. 300° C.), at 46 per cent. bismuth (M.pt. 180° C.), and at 78 per cent. bismuth (M.pt. 200° C.). There are three ranges of solid solution: α between 0 and 4 per cent. bismuth, β between 5.5 and 32 per cent. bismuth, and γ between 57 and 65 per cent. bismuth. The last contains the compound Tl_3Bi_5 . This compound becomes superconducting⁶ at -266.8° C.

Bismuth-Silicon.⁷—In this system, within the range of composition between 2 and approximately 100 per cent. silicon the melt, above 1415° C., consists of two immiscible liquids. A eutectic is formed at 0.8 per cent. silicon (M.pt. 264° C.). Solid solution occurs to only a very slight extent.

Bismuth-Cerium.⁸—The following compounds are formed: Ce_3Bi (decomposing at 1395° C.), Ce_4Bi_3 (M.pt. 1630° C.), $CeBi$ (decomposing at 1520° C.) and $CeBi_2$ (decomposing at 870° C.). Eutectics are found at 5.3 per cent. bismuth (M.pt. 757° C.) and at approximately 100 per cent. bismuth (M.pt. 270° C.). Discontinuities occur on the liquidus curve at 33 per cent. bismuth (1359° C.), at 69 per cent. bismuth (1520° C.) and at 82 per cent. bismuth (870° C.).

Bismuth-Tin.⁹—A eutectic occurs at 58 per cent. tin (M.pt. 135° C.),

¹ Fischer, *Zeitsch. technische Physik*, 1925, 6, 146; Tammann and Heinzel, *Zeitsch. anorg. Chem.*, 1928, 176, 147.

² Pushin, *Zeitsch. anorg. Chem.*, 1903, 36, 201.

³ Gwyer, *Zeitsch. anorg. Chem.*, 1906, 49, 311; Hansen and Blumenthal, *Metallwirtschaft*, 1931, 10, 925.

⁴ Pushin, Stepanovic and Stajic, *Zeitsch. anorg. Chem.*, 1932, 209, 329; Kroll, *Metallwirtschaft*, 1932, 11, 435.

⁵ Kurnakov and Ageeva, *Ann. Inst. Anal. Phys. Chem.*, 1935, 7, 49; Olander, *Zeitsch. Krist.*, 1934, 89, 89; *Zeitsch. physikal. Chem.*, 1934, 169, 260; Kurnakov, Zhemchuzhnyi and Tararin, *Zeitsch. anorg. Chem.*, 1914, 83, 200.

⁶ de Haas, *Metallwirtschaft*, 1930, 9, 149; *Naturwissenschaften*, 1929, 17, 85; de Haas, van Aubel and Voogd, *Verslag. Akad. Wetenschappen Amsterdam*, 1928, 37, 706.

⁷ Ehret and Abramson, *J. Amer. Chem. Soc.*, 1934, 56, 385; Jette and Gebert, *J. Chem. Physics*, 1933, 1, 753; Williams, *Zeitsch. anorg. Chem.*, 1907, 55, 1.

⁸ Vogel, *ibid.*, 1914, 84, 323.

⁹ Thomas and Evans, *Phil. Mag.*, 1934, 17, 65; Bucher, *Zeitsch. anorg. Chem.*, 1916, 98, 97; Kapp, *Ann. Physik*, 1901, 6, 754; Solomon and Morris Jones, *Phil. Mag.*, 1931, 11, 1090.

and there is probably a eutectoid at 96 per cent. tin (forming at 95°C). The solid solubility of tin in bismuth and of bismuth in tin is probably less than 1 per cent. in each case. The eutectic mixture becomes superconducting¹ at -269.24°C .

Bismuth-Lead.²—There are no intermetallic compounds. A eutectic is formed at 58 per cent. bismuth (M.pt. 125°C). The solid solubility of bismuth in lead is 37 per cent. at 125°C . and 16 per cent. at 0°C . The solid solubility of lead in bismuth is 2.7 per cent. at 125°C . and slightly less at 0°C . The eutectic mixture becomes superconducting at a temperature slightly above the boiling point of helium.³ The hardening effect of bismuth on lead is less than that of antimony.⁴

Bismuth-Antimony.⁵—These metals form a continuous series of solid solutions. The liquidus curve lies wholly between the melting points of the component metals, and the solidus is horizontal within the range of composition lying between 40 and 100 per cent. bismuth. X-ray analysis indicates that these alloys crystallise with a face-centred, rhombohedral structure; the lattice edge varies almost linearly with the composition. (See p. 42.)

Bismuth-Selenium.⁶—Two compounds are formed, BiSe (decomposing at 602°C .) and Bi_2Se_3 (M.pt. 688°C). Above 608°C . and within the range of composition between 50 and 92 per cent. selenium the melt consists of two immiscible liquids. Eutectics are formed at approximately pure bismuth and pure selenium. (See fig. 10.)

Bismuth-Tellurium.⁷—One compound only, Bi_2Te_3 (M.pt. 573°C .), is formed. Eutectics occur at 15 per cent. bismuth (M.pt. 370°C .) and at 98.8 per cent. bismuth (M.pt. 253°C .). The compound Bi_2Te_3 forms solid solutions with both of the elements. (See fig. 10.)

Bismuth-Manganese.⁸—A eutectic is formed at 1.3 per cent. manganese (M.pt. 263°C .). Above 1240°C . and within the range of composition from 42 to approximately 100 per cent. manganese the melt consists of two immiscible liquids. Discontinuities occur on the liquidus curve at 8.3 per cent. manganese (453°C .) and at 42 per cent. manganese (1240°C .).

Bismuth-Iron.⁹—These metals are mutually insoluble in each other in the solid state, and they do not combine with one another. The addition of bismuth to cast-iron produces softening and a reduction of strength; the softening is accompanied by decomposition of the carbides.¹⁰

¹ de Haas, *Metallwirtschaft*, 1930, 9, 149.

² Cowan, Hiers and Edwards, *A.S.S.T.*, "National Metals Handbook," 1930, 718; Thomson, *Bureau of Standards J. Research*, 1930, 5, 1085; Honda and Ishigaki, *Sci. Rep. Tohoku Imp. Univ.*, 1925, 14, 219; Herold, *Zeitsch. anorg. Chem.*, 1920, 112, 131; Guertler, "Metallography" (Berlin), 1910; Solomon and Morris Jones, *loc. cit.*

³ de Haas, *Metallwirtschaft*, 1930, 9, 149.

⁴ For the properties of alloys of bismuth and lead, see also di Capua and Arnone, *Atti R. Accad. Lincei*, 1924, [5], 33, 28; Mallock, *Nature*, 1928, 121, 827.

⁵ Cook, *J. Inst. Metals*, 1922, 28, 421; Bowen and Morris Jones, *Phil. Mag.*, 1932, 13, 1029. See also Masing and Overlach, *Wiss. Veröff. Siemens Konzern*, 1930, 9, 331.

⁶ Parravano, *Gazzetta*, 1913, 43 I, 201; Parravano and Caglioti, *ibid.*, 1930, 60, 923.

⁷ Mönkemeyer, *Zeitsch. anorg. Chem.*, 1905, 46, 415; Körber and Haschimoto, *Zeitsch. anorg. Chem.*, 1930, 188 (Schenck-Festschr.), 114.

⁸ Parravano and Perret, *Gazzetta*, 1915, 45 I, 390.

⁹ Hägg, *Nova Acta Regia Soc. Sci. Upsaliensis*, 1929, [4], 7, No. 1; *Zeitsch. Krist.*, 1928, 68, 470. See also Heinzel, *Zeitsch. technische Physik*, 1929, 10, 136.

¹⁰ Smith and Aufderhaar, *Iron Age*, 1931, 123, 96.

Bismuth-Cobalt.¹—A eutectic is formed at 97 per cent. bismuth (M.pt. 260° C.). Above 1350° C. and within the range of composition from 9 to 95 per cent. bismuth the melt consists of two immiscible liquids.

Bismuth-Nickel.²—Two compounds are formed, NiBi₃ (decomposing at 560° C.) and NiBi (decomposing at 720° C.). There is a eutectic at 0.7 per cent. nickel. Discontinuities occur on the liquidus curve at 4 per cent. nickel (560° C.) and 12 per cent. nickel (720° C.). The solid solubility of bismuth in nickel is 5 per cent. ; this solid solution is magnetic below the temperature range from 360° to 396° C.

Bismuth-Rhodium.³—Three compounds are formed, RhBi₄, RhBi₂ and RhBi. At 433° C. the compound RhBi₄ is decomposed and RhBi₂ formed. There are three eutectics, at 7 per cent. rhodium (M.pt. 260° C.), at 19.8 per cent. rhodium (M.pt. 772° C.), and at 31.5 per cent. rhodium (M.pt. 995° C.).

A few ternary alloy systems containing bismuth as one of the components have also been investigated. Among them may be mentioned the systems **bismuth-zinc-cadmium**,⁴ **bismuth-tin-zinc**,⁵ and **bismuth-tin-lead**.⁶ In the last system a ternary eutectic is formed containing 52 per cent. bismuth, 16 per cent. tin and 32 per cent. lead ; it melts at 96° C. It has also been suggested that a ternary compound, Bi₂SnPb, is formed as a result of a reaction in the solid phase. This compound is stable below 76° C., but above that temperature it decomposes, forming three solid solutions.⁷

The quaternary system **bismuth-cadmium-tin-lead** has also been investigated.⁸ A quaternary eutectic is formed containing 49.5 per cent. bismuth, 10.10 per cent. cadmium, 13.13 per cent. tin and 27.27 per cent. lead. It melts at 70° C. (See table, p. 149.)

¹ Lewconja, *Zeitsch. anorg. Chem.*, 1908, 59, 293.

² Voss, *ibid.*, 1908, 57, 34; Hägg and Funke, *Zeitsch. physikal. Chem.*, 1930, 6, 272.

³ Rode, *Ann. Inst. Platine*, 1929, No. 7, 21.

⁴ Mathewson and Scott, *Zeitsch. Metallkunde*, 1914, 5, 1.

⁵ Muzaffar, *J. Chem. Soc.*, 1923, 123, 2341.

⁶ Mazzotto, *Zeitsch. Metallkunde*, 1913, 4, 273; Shepherd, *J. Phys. Chem.*, 1902, 6, 519; Charpy, *Compt. rend.*, 1898, 126, 1569.

⁷ Ishihara, *Sci. Rep. Tohoku Imp. Univ.*, 1929, 18, 715.

⁸ Parravano and Sirovich, *Gazzetta*, 1912, 42 1, 630; Hommel, *Zeitsch. Metallkunde*, 1921, 13, 511, 565.

CHAPTER IV.

COMPOUNDS OF BISMUTH.

General.—In accordance with its position in the Periodic Table, bismuth shows more metallic properties than any other element of this sub-group; it resembles the other members in showing variable valency, but compounds other than trivalent are, in general, either unstable or of doubtful existence. Five oxides have been described, viz. bismuth monoxide Bi_2O_2 , trioxide Bi_2O_3 , tetroxide Bi_2O_4 , pentoxide Bi_2O_5 , and hexoxide Bi_2O_6 . The lower oxides are definitely basic, although only the halides and some organic compounds of bivalent bismuth have been described, while the higher oxides show feeble acidic properties. No definite acid has been isolated, but alkali bismuthates, derived from quadri- and quinquevalent bismuth, have been prepared. These are, however, very unstable, being decomposed by water with evolution of oxygen. Salts of trivalent bismuth are readily hydrolysed by water, many intermediate products of great complexity being formed, the structure and composition of which are still to some extent uncertain; the hydrolysis is, however, incomplete, as the final product is, in each case, an oxy-salt of the type BiOX , e.g. BiOCl . A characteristic feature of trivalent compounds, particularly the halides, is the tendency to form complex compounds with halogen acids. In these complexes the bismuth atom appears to become quinquevalent and to enter a complex anion.¹

The Physiological Action of Bismuth and its Compounds.—Bismuth compounds are not appreciably absorbed into the system when taken internally; absorption appears to take place more readily, however, when applied externally, as in a dusting powder. The salts are used mainly on account of their local action. Bismuth subnitrate (bismuthyl nitrate) is considered to be an astringent and an antiseptic, its action probably being due to hydrolysis causing the liberation of nitric acid.

When taken by the mouth, bismuth preparations form a protective coating on the stomach and intestines. They are used largely in the treatment of gastric affections and diarrhoea. Recently they have been used in the treatment of syphilis and similar diseases, sodium potassium bismuthyl tartrate being most commonly employed. Bismuth oleate is used for intramuscular injections.

Bismuth subnitrate is believed to lessen the secretion of acid in the stomach; it has been known to cause constipation.

Bismuth, when absorbed, is stored up in the liver.

¹ Müller and Kürthy, *Biochem. Zeit.*, 1924, 147, 385; Jellinek and Kühn, *Zeitsch. physikal. Chem.*, 1923, 105, 337; Noyes, Hall and Beattie, *J. Amer. Chem. Soc.*, 1917, 39, 2526.

Large quantities of bismuth can be administered without producing poisoning symptoms. Cases of poisoning have been reported, though in the older cases the poisoning was probably due to impurities, such as arsenic, in the bismuth. Cases of poisoning are indicated first by ulcerations in the mouth, followed by vomiting and diarrhoea. Death ensues very rarely.¹

BISMUTH AND HYDROGEN.

From the position of bismuth in the Periodic Table it is to be expected that a stable hydride of bismuth would be formed only with difficulty. Until comparatively recently the existence of bismuth hydride was doubtful, but later investigations have revealed that a gaseous trihydride can exist, and that it resembles in many ways the trihydrides of antimony and arsenic. A solid hydride has also been reported.² Hydrogen is not absorbed by bismuth in the electric discharge tube.³

A substance described as **bismuth dihydride**, Bi_2H_2 , has been obtained by the action of zinc and hydrochloric acid upon bismuth trichloride. It is a grey solid which decomposes when heated *in vacuo* or in a current of hydrogen.⁴ The true nature of this substance is, however, not fully established.⁵

Bismuth Trihydride, BiH_3 , was first obtained in small quantities by the action of dilute hydrochloric acid (0.2*N*) on an alloy of magnesium and thorium C (a radioactive isotope of bismuth).⁶ It has since been obtained from a non-radio alloy of bismuth and magnesium by the action of more concentrated hydrochloric acid (4*N*). The best results appear to be obtained when the magnesium is not completely alloyed with the bismuth but only superficially coated with that metal.⁷ With non-radio material approximately 5×10^{-5} of the bismuth used is converted into the hydride; this is about one-twentieth of the yield obtained when radio materials are employed. The formation of the trihydride could not be detected when active hydrogen reacted with powdered bismuth.⁸ It is formed by an oscillating discharge between bismuth electrodes in an atmosphere of hydrogen.⁹ In the latter method it is essential that the products should be removed and cooled to room temperature as rapidly as possible, and there must be a complete absence of organic substances.

Bismuth trihydride is a gaseous compound¹⁰ which is almost as stable as antimony trihydride at ordinary temperatures but is readily

¹ Dixon, "Manual of Pharmacology" (London, 1929), 7th Ed., 408; Cushny, "A Text-Book of Pharmacology and Therapeutics," translated by Edmunds and Gunn (London, 1928), 9th Ed., 673. For bibliography, see Anon, *Analyst*, 1933, 58, 607.

² For early references to bismuth hydride, see Ruhland, *Schweigger's J.*, 1815, 15, 417; Meurer, *Arch. Pharm.*, 1843, [2], 36, 33; Schlossberger and Fresenius, *Annalen*, 1844, 51, 418.

³ Newman, *Proc. Phys. Soc. London*, 1921, 33, 73.

⁴ Weekes and Druce, *Rec. Trav. chim.*, 1925, 44, 970; *J. Chem. Soc.*, 1925, 127, 1799; *Nature*, 1925, 116, 710.

⁵ Strecker and Daniel, *Ber.*, 1926, 59 B, 1691; Weekes and Druce, *Chem. News*, 1926, 133, 243.

⁶ Paneth, *Ber.*, 1918, 51, 1704; *Zeitsch. Elektrochem.*, 1918, 24, 298.

⁷ Paneth and Winternitz, *Ber.*, 1918, 51, 1704, 1728.

⁸ Pearson, Robinson and Stoddart, *Proc. Roy. Soc.*, 1933, 142 A, 275.

⁹ Foresti and Mascaretti, *Gazzetta*, 1930, 60, 745. See also Paneth, Matthies and Schmidt-Hebbel, *Ber.*, 1922, 55 B, 775.

¹⁰ For the spectrum of bismuth hydride, see Hulthén and Heimer, *Nature*, 1931, 127, 557; 1932, 129, 399; Hulthén, *ibid.*, 1932, 129, 56.

decomposed on heating. At 160° C. the amount of undecomposed hydride is 35 per cent., at 250° C. 9 per cent. and at 350° C. 6 to 7 per cent. At red heat decomposition is complete. In the heated tube employed in the Marsh test, a mirror similar to the antimony mirror is produced: a strong brown mirror is obtained in front of the heated spot and a fainter ring behind it. The hydride is completely decomposed by concentrated sulphuric acid. The best absorption reagent for the gas is 0.4*N* solution of silver nitrate; it is also partially absorbed by normal potassium hydroxide solution, 0.4*N* solution of sodium carbonate, 4*N* solution of sulphuric acid, and water saturated with hydrogen sulphide. Drying agents such as soda-lime and calcium chloride may also be used for its absorption, but water alone does not absorb it well.

Bismuth trihydride can be distinguished from antimony trihydride by a luminescence method.¹ The gas from the Marsh test is ignited, and bismuth is deposited on a small fragment of calcium carbonate held in the flame. If the calcium carbonate, after cooling, is placed on the edge of a hydrogen flame the bismuth on it will impart to the flame a cornflower blue coloration. Antimony in similar circumstances imparts an azure blue coloration.²

BISMUTH AND THE HALOGENS.

In the principal compounds of bismuth with the halogens, the bismuth is tervalent. It is possible that an unstable pentafluoride, or an oxy-trifluoride, exists at low temperatures, but there is no evidence

HALIDES AND OXYHALIDES OF BISMUTH.

Fluorine.	Chlorine.	Bromine.	Iodine.
	[BiCl ₂]	[BiBr ₂]	[BiI ₂]
BiF ₃	BiCl ₃ [HBiCl ₄]	BiBr ₃ [HBiBr ₄]	BiI ₃ [HBiI ₄]
H ₃ BiF ₆	[H ₂ BiCl ₅] [HBi ₂ Cl ₇]	[H ₂ BiBr ₅]	[H ₂ BiI ₅] [H ₃ Bi ₂ I ₉]
BiOF BiOF.2HF	BiOCl [Bi ₂ O ₃ Cl ₂] [Bi ₃ O ₂ Cl ₃] [Bi ₄ O ₃ Cl ₄]	BiOBr	BiOI [Bi ₅ O ₃ I ₄]
[BiF ₅] [BiOF ₃]		[Bi ₅ O ₁₅ Br ₆] [Bi ₁₁ O ₁₃ Br ₇]	

¹ Paneth and Winternitz, *loc. cit.*

² See also Mugellini, *Boll. Chim. farm.*, 1929, 68, 1086; Paneth, Johannsen and Matthies, *Ber.*, 1922, 55 B, 769; Paneth, *Zeitsch. Elektrochem.*, 1920, 26, 452; Vanino and Zumbusch, *Arch. Pharm.*, 1911, 249, 483. For a comparison of the properties of the hydrides of elements of the fifth group, see Durrant, Pearson and Robinson, *J. Chem. Soc.*, 1934, 137, 730; Pearson and Robinson, *ibid.*, p. 736.

for the existence of other quinquivalent compounds except perhaps in complexes. Bivalent compounds of bismuth with the halogens (with the exception of fluorine) have been reported, but it is doubtful if these have been obtained in a pure state, and they are not very stable. With the exception of the fluorides, the halides are all hydrolysed by water, but the hydrolysis is not complete, the final product being an oxyhalide. The halides tend to form complexes with the corresponding halogen acid; these complexes are themselves acidic, and in all cases except the fluoride, stable salts have been obtained.

Bismuth and Fluorine.

Of the two fluorides of bismuth that have been reported, the trifluoride is the only one known to exist with certainty. It is possible that an unstable pentafluoride may exist at low temperatures, but it has not yet been isolated.

Bismuth Trifluoride, BiF_3 , is obtained by the addition of a concentrated solution of potassium fluoride to a neutral solution of bismuth nitrate; ¹ or by the action of hydrofluoric acid upon bismuth trioxide.² In the latter case the mixture is warmed, and hydrofluoric acid is added as evaporation takes place. When the action ceases, the liquid is decanted and evaporated; the residue is then heated until no more fumes of hydrofluoric acid are evolved.

Bismuth trifluoride is a heavy, greyish-white, crystalline powder. The crystal has a face-centred cubic structure with four molecules in the unit cell:³

$$a = 5.853 \pm 0.004 \text{ \AA.}$$

Its density⁴ is 5.32 at 20° C. It is the most stable halide of bismuth. It melts without decomposition and is only slightly volatile even when strongly heated. It is almost insoluble in both water and alcohol, and is not hydrolysed by cold or boiling water.⁵ It is decomposed by, and dissolves in, hot mineral acids.⁶ It does not react with sulphur, or with the oxides of nitrogen. It dissolves readily on boiling in a concentrated solution of potassium fluoride, but it has not been possible to isolate a complex salt from this solution.⁷

If, when preparing bismuth trifluoride by the action of hydrofluoric acid upon bismuth hydroxide, the residue is only gently heated, a substance is produced which appears to be a complex **hydrofluobismuthic acid**, H_3BiF_6 or $\text{BiF}_3 \cdot 3\text{HF}$. It is a greyish-white, crystalline, deliquescent substance; on heating it loses hydrofluoric acid, and on heating with water it is decomposed with the formation of bismuthyl fluoride, BiOF , an intermediate compound $\text{BiOF} \cdot 2\text{HF}$ being formed, which is decomposed on washing with water.⁸ No salts of this acid are known.

If a boiling concentrated solution of ammonium fluoride is saturated with precipitated bismuth hydroxide, and the solution allowed to stand

¹ Gott and Muir, *Chem. News*, 1887, 56, 257; *J. Chem. Soc.*, 1888, 53, 137.

² Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 33.

³ Hassel and Nilssen, *Zeitsch. anorg. Chem.*, 1929, 181, 172.

⁴ The density calculated from crystal structure is stated to be 8.75.

⁵ Herz and Bulla, *Zeitsch. anorg. Chem.*, 1909, 61, 387.

⁶ Fullerton, *Amer. J. Sci.*, 1877, [3], 14, 281.

⁷ von Helmont, *Zeitsch. anorg. Chem.*, 1893, 3, 143.

⁸ Muir, Hoffmeister and Robbs, *loc. cit.*

for a long time, on cooling, small, transparent, rhombic or monoclinic crystals of **ammonium fluobismuthate** or **bismuth ammonium fluoride**, $(\text{NH}_4)\text{BiF}_4$, separate out. The crystals are easily decomposed by water, yielding bismuthyl fluoride; and they dissolve in hot moderately dilute acids.¹

Bismuthyl Fluoride or *Bismuth Oxyfluoride*, BiOF , can be obtained by the decomposition of $\text{BiF}_3 \cdot 3\text{HF}$ or of $\text{BiOF} \cdot 2\text{HF}$ as described above; or by adding freshly precipitated bismuth hydroxide to hydrofluoric acid until the acid is just neutralised.² It is described as a heavy, white powder, of density 7.5 at 20° C., not deliquescent, decomposed when heated to bright redness.

Bismuth trifluoride does not combine with fluorine except perhaps in traces at -80° C.³ If so-called "bismuthic acid" or potassium bismuthate is added to 40 per cent. hydrofluoric acid at -10° C., a colourless, very unstable solution is obtained which probably contains a compound of quinquivalent bismuth.⁴ The compound has not been isolated, as it decomposes when the solution is evaporated. It may be **bismuth pentafluoride**, BiF_5 , but it appears more probable that it is mainly **bismuth oxytrifluoride**, BiOF_3 . The solution has strong oxidising properties, as shown by its action on hydrochloric acid, potassium iodide and alcohol (the latter being oxidised to aldehyde). If potassium fluoride is added to the solution before evaporation, the substance $\text{Bi}_3\text{O}_4\text{F}_7 \cdot 3\text{KF}$ separates out as small, yellow crystals; with excess of potassium fluoride, a double compound of bismuth oxytrifluoride and potassium fluoride, $\text{BiOF}_3 \cdot 3\text{KF}$, is obtained as well-formed, colourless, prismatic crystals which decompose in moist air, becoming yellow.

Bismuth and Chlorine.

Although the chief compound of bismuth and chlorine is bismuth trichloride, BiCl_3 , many of the older investigators held that a lower chloride, **bismuth dichloride**, BiCl_2 or Bi_2Cl_4 , also existed. It is stated that this compound is formed as a black substance when a slow current of chlorine is passed over powdered bismuth heated nearly to the melting point; after prolonged treatment it changes to a light amber liquid from which the trichloride can be obtained by sublimation.⁵ It is claimed that bismuth dichloride may also be obtained by heating a mixture of bismuth and mercurous chloride to between 230° and 250° C., by heating bismuth ammonium chloride in a current of hydrogen at 300° C.,⁶ by the reduction of bismuth trichloride by bismuth, phosphorus, zinc, tin, mercury and certain organic compounds⁷ or by hydrogen,⁸ and by heating bismuth trichloride with phosphorus trichloride.⁹ More recently, thermal investigations of the system $\text{Bi}-\text{BiCl}_3$ have been undertaken, but the evidence obtained concerning the existence of the

¹ von Helmont, *loc. cit.*

² Gott and Muir, *loc. cit.*

³ Ruff, Knoch and Zedner, *Zeitsch. anorg. Chem.*, 1908, 57, 320.

⁴ Weinland and Lauenstein, *Zeitsch. anorg. Chem.*, 1899, 20, 46.

⁵ Muir, *J. Chem. Soc.*, 1876, 29, 144; Weber, *Pogg. Annalen*, 1859, 107, 596; Dehéran, *Bull. Soc. chim.*, 1862, [I], 4, 22; Thomas, *Ann. Chim. Phys.*, 1898, [7], 13, 145.

⁶ Schneider, *Pogg. Annalen*, 1855, 96, 130.

⁷ Weber, *loc. cit.*

⁸ Muir, *loc. cit.* See also, however, Heintz, *Pogg. Annalen*, 1844, 63, 55.

⁹ Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 454.

dichloride is conflicting. Herz and Guttman found a maximum on the liquidus curve at a composition corresponding to BiCl_2 , the melting point being 163°C. and the density 4.85 to 4.88 (the latter value being lower than the density of the equivalent mixture of bismuth and bismuth trichloride);¹ while Eggink could find no evidence for the existence of BiCl_2 but suggested that both BiCl and BiCl_4 (see fig. 5) were formed.² According to Marino and Becarelli, the so-called bismuth dichloride is really a solid solution; but although the melting point of this solution is higher than that of either bismuth or bismuth

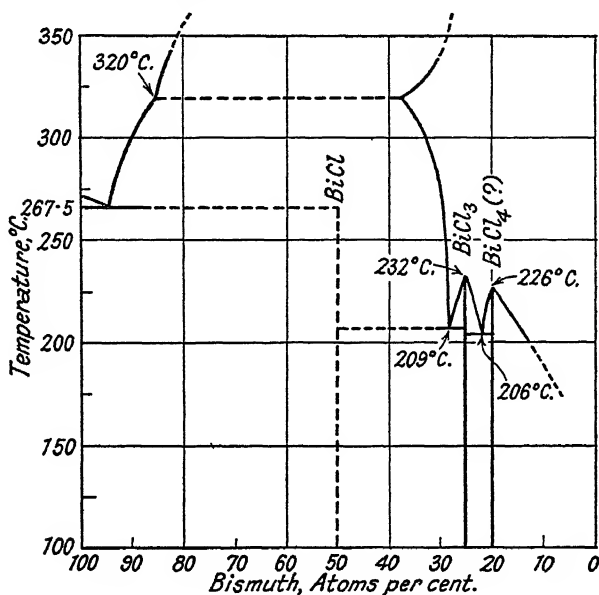


FIG. 5.—Freezing Point Curve of the System Bismuth-Chlorine.

trichloride, they were unable to determine any maxima on the liquidus curve on account of sublimation. This solid solution undergoes a transformation into a β -variety, the change being accompanied by a marked evolution of heat; on fusion and cooling, these β -crystals change into α -crystals of different composition and two liquid phases separate out.³ An investigation into the free energy of fused bismuth trichloride did not afford any evidence in favour of the existence of a lower chloride.⁴

The compound has certainly not been obtained pure, although by cooling the melt obtained by heating bismuth trichloride with bismuth, black, needle-shaped crystals have been obtained.⁵ The impure substance is dull black, and very hygroscopic; it melts readily. Many of the reactions ascribed to it could almost equally well be ascribed to a mixture of bismuth and its trichloride. When heated to about 300°C.

¹ Herz and Guttman, *Zeitsch. anorg. Chem.*, 1908, 56, 422.

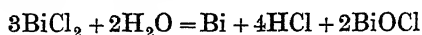
² Eggink, *Zeitsch. physikal. Chem.*, 1908, 64, 449. See also Herz, *Zeitsch. anorg. Chem.*, 1909, 61, 119.

³ Marino and Becarelli, *Atti R. Accad. Lincei*, 1915, [v], 24, ii, 625; 1916, [v], 25, i, 221, 326.

⁴ Devoto and Guzzi, *Gazzetta*, 1929, 59, 708.

⁵ Weber, *loc. cit.*

in the absence of air the substance decomposes into bismuth and bismuth trichloride.¹ Heated in air it forms a mixture of bismuth, bismuth trioxide and bismuthyl chloride.² It is readily decomposed by water according to the equation



It combines with chlorine to form the trichloride. With a concentrated solution of potassium hydroxide the so-called black bismuth suboxide is obtained, which rapidly oxidises to the yellow trioxide.³ Dilute acids decompose it yielding salts of trivalent bismuth and metallic bismuth.

The substance does not combine with ammonia.⁴ It has been suggested, however, that a double compound with ammonium chloride is formed having the composition $\text{BiCl}_2 \cdot \text{NH}_4\text{Cl}$,⁵ although the dichloride is decomposed by a concentrated solution of ammonium chloride.⁶

Bismuth Trichloride, BiCl_3 , appears to have been prepared first by Boyle in 1664,⁷ and later by Poli in 1713,⁸ by heating a mixture of bismuth and mercuric chloride. It may also be obtained by the direct union of the elements;⁹ by the action of hydrochloric acid upon bismuth in the presence of air,¹⁰ concentrated hydrochloric acid upon bismuth trioxide, pentoxide or trisulphide, or aqua regia upon bismuth;¹¹ by heating bismuth trioxide, pentoxide¹² or trisulphide¹³ in a current of chlorine, the oxides in a current of hydrogen chloride,¹⁴ or bismuth with phosphorus trichloride;¹⁵ or by the action of silicon tetrachloride¹⁶ or sulphur monochloride¹⁷ on bismuth trioxide.

The trichloride is usually prepared by heating bismuth in a rapid current of chlorine and subliming the product in an atmosphere of carbon dioxide; by dissolving bismuth in aqua regia, evaporating the solution to dryness and distilling the residue in an atmosphere of carbon dioxide; or by dissolving bismuth trioxide in hydrochloric acid and proceeding as in the previous method.

Bismuth trichloride forms a snow-white opaque mass which can be crystallised by sublimation, the crystalline mass darkening on exposure to light.¹⁸ Its density¹⁹ is 4.75 at 20° C.; the thermal coefficient of expansion²⁰ between 20° and 120° C. is approximately 167×10^{-6} ; and

¹ Schneider, *loc. cit.*

² Thomas, *loc. cit.*; Dehérain, *loc. cit.*

³ Schneider, *loc. cit.*

⁴ Dehérain, *loc. cit.*

⁵ Schneider, *loc. cit.*

⁶ Weber, *loc. cit.*

⁷ Boyle, "Experiments and Considerations concerning Colour" (London), 1664.

⁸ Poli, "Mémoires de l'Académie des Sciences" (Paris), 1713, p. 40.

⁹ Davy, *Phil. Trans.*, 1812, 102, 169; Weber, *Pogg. Annalen*, 1859, 107, 596; Dehérain, *Bull. Soc. chim.*, 1862, [1], 4, 22; Muir, *J. Chem. Soc.*, 1876, 29, 144; Cowper, *J. Chem. Soc.*, 1883, 43, 153; Thomsen, *Ber.*, 1883, 16, 40.

¹⁰ Ditte and Metzner, *Compt. rend.*, 1892, 115, 1303; *Ann. Chim. Phys.*, 1893, 29, 389; Heintz, *Pogg. Annalen*, 1844, 63, 55, 559.

¹¹ Tanatar, *Zeitsch. anorg. Chem.*, 1901, 27, 437.

¹² Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 32.

¹³ Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 92; Rammler, *Ber.*, 1891, 24, 354.

¹⁴ Bird Moyer, *J. Amer. Chem. Soc.*, 1897, 18, 1029.

¹⁵ Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 454.

¹⁶ Rauter, *Annalen*, 1892, 270, 251.

¹⁷ Oddo and Serra, *Gazzetta*, 1899, 29, II, 355.

¹⁸ Liesegang, *Photograph. Arch.*, 1893, 34, 177.

¹⁹ Honigschmid and Birckenbach, *Ber.*, 1921, 54 B, 1873.

²⁰ Klemm, Tilk and Müllenheim, *Zeitsch. anorg. Chem.*, 1928, 176, 1.

the molecular volume at low temperatures,¹ calculated from the density at -194°C . and the thermal coefficient of expansion, is 64.2.

The melting point² is 232°C . The density of the molten trichloride varies linearly between 250°C . and 350°C . according to the expression³

$$D_4^t = 4.438 - 0.00229t$$

The surface tension, determined by the method of maximum bubble pressure in an atmosphere of nitrogen, and other data for the density, are as follows :⁴

Temp., $^{\circ}\text{C}$. .	271	304	331	353	382
Density, D_4^t .	3.811	3.735	3.682	3.621	3.554
Surface Tension (dynes per cm.) .	66.2	61.8	58.1	55.3	52.0

The variation of the viscosity of fused bismuth trichloride⁵ with temperature is given below.

Temp., $^{\circ}\text{C}$. .	260	270	280	290	300	310	320	330	340
Viscosity $\times 10^2$ (grams per cm. per sec.) .	32.0	29.5	27.0	25.0	23.0	21.5	20.5	19.0	18.0

The vapour pressure of bismuth trichloride⁶ has been determined, and the boiling point⁷ is 447°C . The heat of vaporisation is 18,000 gram-calories per mole.⁸ The vapour density (air=1) is 11.85, the calculated vapour density⁹ being 10.89.

A band spectrum of the vapour of bismuth trichloride has been observed¹⁰ in the region between the wavelengths 4300 Å. and 5500 Å. The emitter appears to be BiCl ; the bands are degraded towards the longer wavelengths, and isotropic effects (due to chlorine) have been observed.

Bismuth trichloride sublimes without decomposition in an atmosphere of carbon dioxide; in air, however, a portion only sublimes

¹ Biltz, Sapper and Wunnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

² *International Critical Tables*, 1926, 1, 106. See also Muir, *J. Chem. Soc.*, 1876, 29, 144.

³ *International Critical Tables*, 1928, 3, 329; Voigt and Biltz, *Zeitsch. anorg. Chem.*, 1924, 133, 277. See also Aten, *Zeitsch. physikal. Chem.*, 1909, 66, 641; Jaeger and Kahn, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 397; Jaeger, *Zeitsch. anorg. Chem.*, 1917, 101, 1.

⁴ Jaeger, *loc. cit.*

⁵ *International Critical Tables*, 1930, 7, 212; Aten, *loc. cit.*

⁶ Evnevitch and Suchodski, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 1503.

⁷ *International Critical Tables*, 1928, 3, 329. See also Maier, *Bureau of Mines Technological Paper*, 1925, 360, 1; Carnelley and Williams, *J. Chem. Soc.*, 1878, 33, 281; Meyer and Krause, *Annalen*, 1891, 264, 124; Anschütz and Weyer, *ibid.*, 1891, 261, 297; Meyer and Freyer, *Zeitsch. anorg. Chem.*, 1892, 2, 4. For the elevation of the boiling point produced by various solutes in bismuth trichloride, see Rügheimer and Rudolf, *Annalen*, 1905, 339, 311.

⁸ Maier, *loc. cit.*

⁹ Jacquelsain, *Ann. Chim. Phys.*, 1837, [2], 66, 113; *J. prakt. Chem.*, 1838, 14, 1.

¹⁰ Saper, *Phys. Review*, 1931, 37, 1710.

unaltered, the remainder being converted into non-volatile, colourless, mica-like leaflets of bismuth oxychloride.¹

It will dissolve in hydrochloric acid, alcohol, acetone, liquid ammonia,² and to a slight extent in liquid hydrogen sulphide.³ The solution in acetone behaves like an aqueous solution towards many reagents,⁴ and the solution in hydrogen sulphide does not conduct electricity.⁵

The absorption spectrum of very dilute solutions ($N/10,000$) of bismuth trichloride in hydrochloric acid is characterised by a very strong selective action; ⁶ a deep band with its head at $\lambda = 3250$ A. is prominent. Similar solutions of arsenic trichloride and antimony trichloride show general absorption only. The Raman spectrum of a solution of bismuth trichloride in hydrochloric acid consists of four lines, the fourth of which is exceptionally strong.⁷

The heat of formation of the trichloride from the elements ⁸ is 90,680 gram-calories per mole.

The reduction of bismuth trichloride has already been discussed (p. 158). In addition to the reactions given, reduction may be carried out by passing the vapour of the trichloride over magnesium heated to the melting point; metallic bismuth is precipitated.⁹

The trichloride is deliquescent, and is decomposed by water forming bismuth oxychloride; ¹⁰ with excess of water the reaction is complete, whilst it is hindered by the presence of hydrochloric acid or alkali chlorides.¹¹

No reaction takes place when bismuth trichloride is heated with sulphur monochloride or chromyl chloride.¹²

Bismuth trichloride reacts immediately with liquid hydrogen sulphide, even at low temperatures, forming an orange-red solid, which, after drying in a desiccator over sulphuric acid, has the formula $\text{BiSCl} \cdot \text{BiCl}_3$.¹³

The trichloride reacts with hydrogen sulphide in the dry way with the formation of bismuth thiochloride, BiSCl .¹⁴ Bismuth thiophosphate, BiPS_4 , is formed by the action of phosphorus pentasulphide.¹⁵

When heated in nitric oxide, bismuth trichloride forms a yellow crystalline substance $\text{BiCl}_3 \cdot \text{NO}$, which is decomposed by water.¹⁶ This substance can be melted in a sealed tube without decomposition, and is very hygroscopic.¹⁷ Bismuth trichloride also absorbs nitrogen peroxide

¹ Jacquelin, *loc. cit.*

² Gore, *Proc. Roy. Soc.*, 1873, 21, 140.

³ Antoni and Magri, *Gazzetta*, 1905, 35, I, 206.

⁴ Naumann and Schulz, *Ber.*, 1904, 37, 4331.

⁵ Quam and Wilkinson, *Proc. Iowa Acad. Sci.*, 1925, 32, 324.

⁶ Macbeth and Maxwell, *J. Chem. Soc.*, 1923, 123, 370. See also Schäfer and Hein, *Zeitsch. anorg. Chem.*, 1917, 100, 249.

⁷ Daure, *Compt. rend.*, 1928, 187, 940.

⁸ Thomsen, "Thermochemistry" (London), 1908, p. 236.

⁹ Seubert and Schmidt, *Annalen*, 1892, 267, 238; Faktor, *Pharm. Post*, 1904, 38, 153; *Chem. Zentr.*, 1905, 1, 1305.

¹⁰ Jacquelin, *Ann. Chim. Phys.*, 1837, 66, 113; Heintz, *Pogg. Annalen*, 1844, 63, 71; MacIvor, *Chem. News*, 1875, 32, 222; Merz and Weith, *Ber.*, 1880, 13, 210.

¹¹ Causse, *Compt. rend.*, 1891, 112, 1220; 113, 547; *Chem. Zentr.*, 1892, 1, 53.

¹² Muir, *J. Chem. Soc.*, 1878, 33, 193.

¹³ Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258.

¹⁴ Schneider, *Pogg. Annalen*, 1854, 93, 464; Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 90; *Chem. News*, 1895, 71, 35.

¹⁵ Glatsel, *Zeitsch. anorg. Chem.*, 1893, 4, 186.

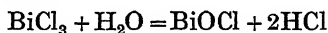
¹⁶ Besson, *Compt. rend.*, 1889, 108, 1012.

¹⁷ Thomas, *Compt. rend.*, 1895, 121, 129.

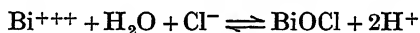
at the ordinary temperature, forming a yellow mass of the composition $\text{BiCl}_3 \cdot \text{NO}_2$, stable in dry air. At higher temperatures this is oxidised, but it does not evolve nitrogen peroxide *in vacuo*. In moist air it is decomposed with evolution of nitrogen peroxide, while water converts it to bismuthyl chloride with a violent evolution of gas.¹ Nitrosyl chloride reacts violently with bismuth trichloride at the ordinary temperature, and from the resulting solution the compound $\text{BiCl}_3 \cdot \text{NOCl}$ separates as an orange-coloured powder, which is deliquescent and decomposed by water.²

The trichloride is converted into trioxide on heating with mercuric oxide.³ It will react with carbon compounds in a manner similar to ferric chloride; it will dissolve in many hydrocarbons, but on heating it is possibly reduced to the dichloride.⁴

Investigation of the hydrolytic dissociation of bismuth trichloride shows that in the reaction



the ratio $\text{BiCl}_3/[\text{HCl}]^2$ remains constant for a considerable range of temperature, but tends to increase somewhat at high concentrations. The presence of alkali chlorides, and more particularly alkali bromides, reduces the extent of dissociation, while alkali nitrates have a smaller influence. Sodium sulphate is practically without influence on the hydrolysis. The effect of increase of temperature is to reduce the amount of dissociation.⁵ From a study of the system $\text{Bi}_2\text{O}_3\text{--HCl--H}_2\text{O}$ (see tables, p. 164) it appears that in certain solutions bismuthyl chloride is the stable phase, in others bismuthyl hydroxide; in the presence of alkali the solid phase BiOCl is quantitatively converted into the hydroxide $\text{BiO} \cdot \text{OH}$ (p. 168). From measurements of the concentrations of the ions H^+ , Cl^- and Bi^{+++} in hydrochloric acid solution saturated with bismuthyl chloride it has been shown that the reaction



obeys the law of mass action.⁶

By dissolving bismuth trioxide in excess of hydrochloric acid and evaporating the solution, fine needle-shaped crystals of *hydrated bismuth trichloride*, $\text{BiCl}_3 \cdot 2\text{H}_2\text{O}$, are deposited.⁷ When water is saturated with bismuth trichloride and hydrochloric acid at 20°C . and cooled to 0°C ., crystals are deposited which have the composition $2\text{BiCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$. These crystals are stable at the ordinary temperature.⁸

Chlorobismuthous Acid.—Bismuth trichloride is very soluble in concentrated hydrochloric acid, and there are indications of the formation of a double compound;⁹ from measurements of the electrical

¹ Thomas, *Compt. rend.*, 1896, 122, 611. See also Besson, *loc. cit.*

² Sudborough, *J. Chem. Soc.*, 1891, 59, 662. See also Rheinboldt and Wasserfuhr, *Ber.*, 1927, 60 B, 732.

³ Volhard, *Ann. Chim. Pharm.*, 1879, 198, 331; Smith and Heyl, *Zeitsch. anorg. Chem.*, 1894, 7, 87.

⁴ Thomas, *loc. cit.*

⁵ Herz and Bulla, *Zeitsch. anorg. Chem.*, 1909, 61, 387; 1909, 63, 59; Dubrisay, *Compt. rend.*, 1909, 148, 830.

⁶ Jellinek and Kuhn, *Zeitsch. physikal. Chem.*, 1923, 105, 337.

⁷ Engel, *Compt. rend.*, 1888, 106, 1797. See also Arppe, *Pogg. Annalen*, 1845, 64, 237; Heintz, *J. prakt. Chem.*, 1848, 45, 102.

⁸ Engel, *Compt. rend.*, 1888, 106, 1797.

⁹ Ditte, *Compt. rend.*, 1880, 91, 986.

EQUILIBRIUM IN THE SYSTEM $\text{Bi}_2\text{O}_3\text{--HCl--H}_2\text{O}$.

Solubility at 18° C.
(Moles per 100 moles Water).

HCl.	Bi_2O_3 .	Solid Phase.
0.71	0.0018	} BiOCl
0.74	0.0021	
0.89	0.0056	
1.18	0.0165	
1.28	0.0247	
1.86	0.0315	
2.20	0.1185	
3.81	0.2835	
Authority: Jellinek and Kühn.		

Solubility (Grams per 100 grams Saturated Solution).

At 25° C.			At 30° C.		
HCl.	Bi_2O_3 .	Solid Phase.	HCl.	Bi_2O_3 .	Solid Phase.
2.50	0.6	BiOCl	2.40	0.60	$\text{BiOCl}\cdot\text{H}_2\text{O}$
4.22	2.60	„	5.69	5.35	„
10.68	11.40	„	13.02	14.52	„
13.43	16.41	„	21.70	30.10	„
18.47	26.42	„	31.50	54.70	„
30.23	50.74	„	32.80	56.00	BiOCl
33.67	58.72	BiCl_3	33.00	58.50	$\text{BiCl}_3\cdot 2\text{H}_2\text{O}$
35.14	58.59	„	33.80	56.60	$\text{BiCl}_3 + \text{BiCl}_3\cdot 2\text{H}_2\text{O}$
			34.90	56.25	BiCl_3
			35.90	55.9	$\text{BiCl}_3\cdot\text{HCl}$
Waris, <i>J. Indian Chem. Soc.</i> , 1925, 1, 307.			Jacobs, <i>Chem. Weekblad.</i> , 1917, 14, 208.		

conductivity of solutions of bismuth trichloride in aqueous hydrochloric acid the composition of this acid would appear to be either HBiCl_4 or H_2BiCl_5 , while investigations using solutions of bismuthyl chloride in hydrochloric acid (see following table) indicate that H_2BiCl_5 predominates when excess of the acid is present in dilute solution, while HBiCl_4 predominates in more concentrated solution with a lower concentration of acid.¹

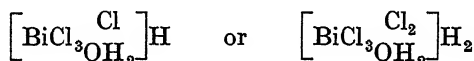
¹ Noyes, Hall and Beattie, *J. Amer. Chem. Soc.*, 1917, 39, 2526.

SOLUBILITY OF BISMUTHYL CHLORIDE IN HYDROCHLORIC ACID AT 25° C.

(Gram-atoms per 1000 grams Water.)

Chlorine Content.	Bismuth Content.	Hydrogen Content (calc.).	Chlorine Content.	Bismuth Content.	Hydrogen Content (calc.).
0.3477	0.00130	0.3438	1.2270	0.1177	0.8746
0.4350	0.00376	0.4237	1.2724	0.1324	0.8752
0.4414	0.00396	0.4295	1.4348	0.1620	0.9488
0.4892	0.00646	0.4698	1.5321	0.1810	0.9891
0.5221	0.00869	0.4960	1.6235	0.2025	1.016
0.5276	0.00899	0.5006	1.6850	0.2050	1.020
0.5796	0.01323	0.5399	1.7706	0.2352	1.065
0.6244	0.01767	0.5714	1.9021	0.2657	1.105
0.6299	0.01856	0.5742	2.5578	0.4216	1.293
0.7038	0.02720	0.6222	3.1865	0.5685	1.481
0.7375	0.03138	0.6434	3.6366	0.6792	1.599
0.7579	0.03473	0.6537	4.2552	0.8324	1.758
0.8824	0.05338	0.7223	4.5056	0.9022	1.799
0.9125	0.05936	0.7343	5.325	1.100	2.025
1.0760	0.08937	0.8079	6.066	1.317	2.115

The true nature of these compounds has not yet been fully ascertained. From physical investigations ¹ it is inferred that the complex may conform to one of the following two formulæ :



Organic compounds corresponding to both of these have been prepared. From the examination of substituted ammonium compounds of chlorobismuthous acid ² it appears possible that three types of organic compounds may exist, to which have been allotted the following names and general formulæ :

- (a) *Hexachlorobismuthites*, $[\text{NH}_3\text{R}]_3[\text{BiCl}_6]$;
- (b) μ -*Dichloro-octachloro-dibismuthites*, $[\text{NHR}_3]_4[\text{Bi}_2\text{Cl}_{10}]$;
- (c) μ -*Trichloro-hexachloro-dibismuthites*, $[\text{NH}_3\text{R}]_3[\text{Bi}_2\text{Cl}_9]$.

The elucidation of the constitution of these compounds is, however, rendered extremely difficult owing to their instability in aqueous solutions.

Chlorobismuthites.—Bismuth trichloride forms a number of complex or double salts with alkali chlorides; some of these are described below. With *lithium* chloride ³ is obtained the compound $2\text{LiCl} \cdot \text{BiCl}_3$. With *sodium* chloride the compound $\text{NaCl} \cdot \text{BiCl}_3 \cdot 3\text{H}_2\text{O}$ is

¹ Schafer and Hein, *Zeitsch. anorg. Chem.*, 1917, 100, 249.

² Gutbier and Müller, *Zeitsch. anorg. Chem.*, 1923, 128, 137.

³ Aloy and Frébault, *Bull. Soc. chim.*, 1906, [3], 35, 396.

formed as a deliquescent substance crystallising in needles; ¹ other sodium compounds that have been described are $2\text{NaCl} \cdot \text{BiCl}_3 \cdot 2\text{H}_2\text{O}$ ² and $2\text{NaCl} \cdot \text{BiCl}_3$. ³ With *potassium* chloride the following compounds are said to exist: $2\text{KCl} \cdot \text{BiCl}_3 \cdot 2\text{H}_2\text{O}$, ⁴ $\text{KCl} \cdot \text{BiCl}_3 \cdot \text{H}_2\text{O}$ ⁵ and $\text{KCl} \cdot \text{BiCl}_3 \cdot 2\text{H}_2\text{O}$. ⁶ The *rubidium* compounds $\text{RbCl} \cdot \text{BiCl}_3 \cdot \text{H}_2\text{O}$ and $\text{RbCl} \cdot \text{BiCl}_3$ have been described; ⁷ also the *cæsium* compounds $3\text{CsCl} \cdot 2\text{BiCl}_3$ and $3\text{CsCl} \cdot \text{BiCl}_3$. ⁸ With *thallium* chloride the compounds $3\text{TlCl} \cdot \text{BiCl}_3$ and $6\text{TlCl} \cdot \text{BiCl}_3$ have been obtained, both in the form of large, thin, colourless plates. ⁹ Mixed halogen compounds of bismuth chloride and potassium halides have also been described, among them being $\text{KBr} \cdot \text{KCl} \cdot \text{BiCl}_3$, $2\text{KBr} \cdot \text{BiCl}_3$. ¹⁰

The following compounds with *ammonium* chloride have been described: The hydrate $2\text{NH}_4\text{Cl} \cdot \text{BiCl}_3 \cdot 2\text{H}_2\text{O}$ forms crystals of the rhombic system, isomorphous with those of the corresponding bromide and those of the potassium double salt; ¹¹ the anhydrous salt forms double six-sided pyramids, and is isomorphous with the corresponding antimony compound. ¹² The compound $3\text{NH}_4\text{Cl} \cdot \text{BiCl}_3$ forms large, tabular crystals of the rhombic system. ¹³ Another compound, to which the formula $5\text{NH}_4\text{Cl} \cdot 2\text{BiCl}_3$ has been given, is probably formed as one of the products when a solution containing equimolecular proportions of ammonium chloride and bismuth trichloride is crystallised (the other product being $2\text{NH}_4\text{Cl} \cdot \text{BiCl}_3$, described above); this compound forms fine, tabular crystals of the rhombohedral system. ¹⁴

A systematic investigation of the compounds of bismuth trichloride with chlorides of bivalent metals revealed the following types of compounds: (1) $\text{BiCl}_3 \cdot \text{M}'\text{Cl}_2$, corresponding with the series $\text{BiCl}_3 \cdot 2\text{M}'\text{Cl}$ (where M' is an alkali metal); salts of this type are regarded as derivatives of pentachlorobismuthous acid, $\text{H}_2[\text{BiCl}_5]$. The following have been examined: $\text{BiCl}_3 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$, stout, rectangular plates; $\text{BiCl}_3 \cdot \text{BaCl}_2 \cdot 4\text{H}_2\text{O}$, rhombic plates; $\text{BiCl}_3 \cdot \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, pale red prisms; $\text{BiCl}_3 \cdot \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, green needles. (2) $2\text{BiCl}_3 \cdot \text{M}'\text{Cl}_2$, corresponding to the series $\text{BiCl}_3 \cdot \text{M}'\text{Cl}$ (where M' is an alkali metal); salts of this type are regarded as derivatives of tetrachlorobismuthous acid, $\text{H}[\text{BiCl}_4]$. The following have been examined: $2\text{BiCl}_3 \cdot \text{CaCl}_2 \cdot 7\text{H}_2\text{O}$, colourless needles; $2\text{BiCl}_3 \cdot \text{SrCl}_2 \cdot 7\text{H}_2\text{O}$, stout needles; $2\text{BiCl}_3 \cdot \text{BaCl}_2 \cdot 5\text{H}_2\text{O}$, slender needles. (3) $4\text{BiCl}_3 \cdot \text{M}'\text{Cl}_2$, corresponding with the series $2\text{BiCl}_3 \cdot \text{M}'\text{Cl}$ (where M' is an alkali metal); salts of this type are regarded as derivatives of heptachlorodibismuthous acid, $\text{H}[\text{Bi}_2\text{Cl}_7]$. The following have been

¹ Jacquelin, *J. prakt. Chem.*, 1838, 14, 1.

² Pliny Brigham, *J. Amer. Chem. Soc.*, 1892, 14, 164.

³ Aloy and Frébault, *loc. cit.*

⁴ Aloy and Frébault, *loc. cit.*

⁵ Remsen, *J. Amer. Chem. Soc.*, 1892, 14, 81.

⁶ Pliny Brigham, *loc. cit.*

⁷ Pliny Brigham, *loc. cit.*

⁸ Remsen, *loc. cit.*

⁹ Ephraim and Barteczko, *Zeitsch. anorg. Chem.*, 1909, 61, 238. See also Scarpa, *Atti R. Accad. Lincei*, 1912, [v], 21, ii, 719. For compounds with chlorides of the alkali metals, see also Arppe, *Pogg. Annalen*, 1845, 64, 237; Rammelsberg, *ibid.*, 1859, 106, 105.

¹⁰ Field, *J. Chem. Soc.*, 1893, 63, 540; Atkinson, *ibid.*, 1883, 43, 289.

¹¹ Rammelsberg, "*Handbuch Kryst. Chem.*," 1855, 215; *Pogg. Annalen*, 1859, 106, 147; Groth, *Chem. Kryst.*, 1906, I, 431.

¹² Jacquelin, *Ann. Chim. Phys.*, 1832, [2], 66, 113. See also Dehérain, *loc. cit.*

¹³ Arppe, *Pogg. Annalen*, 1845, 64, 247.

¹⁴ Rammelsberg, *Pogg. Annalen*, 1859, 106, 147; Groth, *Chem. Kryst.*, 1906, I, 429.

examined: $4\text{BiCl}_3 \cdot \text{MgCl}_2 \cdot 16\text{H}_2\text{O}$, six-sided leaflets; $4\text{BiCl}_3 \cdot \text{SrCl}_2 \cdot 12\text{H}_2\text{O}$, six-sided leaflets; $4\text{BiCl}_3 \cdot \text{MnCl}_2 \cdot 12\text{H}_2\text{O}$, flesh-coloured, six-sided plates; $4\text{BiCl}_3 \cdot \text{FeCl}_2 \cdot 12\text{H}_2\text{O}$, faintly yellowish-red plates; $4\text{BiCl}_3 \cdot \text{CoCl}_2 \cdot 12\text{H}_2\text{O}$, red, six-sided plates; $4\text{BiCl}_3 \cdot \text{NiCl}_2 \cdot 12\text{H}_2\text{O}$, pale green, six-sided plates.¹

Ammoniates.—It has long been known that bismuth trichloride absorbs ammonia when heated gently in its presence,² the reaction yielding one easily volatile addition compound, $\text{BiCl}_3 \cdot 8\text{NH}_3$, and two non-volatile compounds, $2\text{BiCl}_3 \cdot \text{NH}_3$ and $\text{BiCl}_3 \cdot 2\text{NH}_3$.³ $\text{BiCl}_3 \cdot 8\text{NH}_3$ is a colourless substance which volatilises in a current of ammonia; when acted upon by hydrogen chloride it yields the double compound $3\text{NH}_4\text{Cl} \cdot \text{BiCl}_3$. $2\text{BiCl}_3 \cdot \text{NH}_3$ is a red, moderately stable substance which can be melted and crystallised by solidification, but which is attacked by moisture; with hydrogen chloride it forms nearly colourless, deliquescent needles of the double compound $\text{NH}_4\text{Cl} \cdot 2\text{BiCl}_3$. The third compound, $\text{BiCl}_3 \cdot 2\text{NH}_3$, is difficult to obtain pure, usually being mixed with $2\text{BiCl}_3 \cdot \text{NH}_3$. It is a greenish-grey substance, and its composition is deduced from the fact that with hydrogen chloride it forms the compound $2\text{NH}_4\text{Cl} \cdot \text{BiCl}_3$.

With organic bases, bismuth trichloride forms many crystalline complexes.⁴

Attempts to obtain a higher chloride of bismuth by the action of chlorine on molten bismuth trichloride, or by passing chlorine over a heated mixture of bismuthyl chloride and charcoal, have been unsuccessful.⁵

Bismuthyl Chloride, or *Bismuth Oxychloride*, BiOCl .—An oxychloride, which is probably bismuthyl chloride, occurs in the mineral *daubreit*, which is found in Bolivia.⁶

Bismuthyl chloride is the product obtained by the reaction of bismuth trichloride with water, the decomposition being effected by the action of either hot or cold water on the solid, or by the addition of water to a moderately concentrated solution in hydrochloric acid. It is also obtained by the addition of a solution of an alkali chloride to a solution of bismuth nitrate.⁷ Many other methods may also be adopted for the preparation of this substance. (1) When bismuth trichloride is heated in steam, bismuthyl chloride is left as a residue.⁸ (2) It is formed in small quantities when bismuth trichloride is sublimed in air.⁹ (8) It is the stable compound always produced by the action of water, sulphur dioxide, chromyl chloride, nitrogen peroxide and

¹ Weinland, Alber and Schweiger, *Arch. Pharm.*, 1916, 254, 521.

² Persoz, *Ann. Chim. Phys.*, 1830, 44, 315.

³ Dehérain, *Compt. rend.*, 1862, 54, 724. See also Arppe, *Pogg. Annalen*, 1845, 64, 237.

⁴ Vanino and Hauser, *Ber.*, 1900, 33, 2271; 1901, 34, 416; 1902, 35, 663; 1903, 36, 3682; Montemartini, *Gazzetta*, 1900, 30, II, 493; Schiff, *Ber.*, 1901, 34, 804; Vanino and Hartl, *Arch. Pharm.*, 1907, 244, 216; Pastureau, *Compt. rend.*, 1898, 127, 485; Pfeiffer, *Zeitsch. anorg. Chem.*, 1900, 24, 279; Smith, *Ber.*, 1879, 12, 1421.

⁵ Muir, *J. Chem. Soc.*, 1876, 29, 146. See also Hutchins and Lenker, *J. Amer. Chem. Soc.*, 1907, 29, 31.

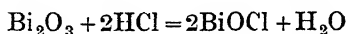
⁶ Domeyko, *Compt. rend.*, 1876, 82, 922.

⁷ Phillips, *Phil. Mag. and Annals*, 1830, 8, 456; Heintz, *Pogg. Annalen*, 1844, 63, 72; Arppe, *ibid.*, 1845, 64, 246; Rose, *ibid.*, 1860, 110, 425; Ruge, *J. prakt. Chem.*, 1865, 96, 133.

⁸ Jacquelin, *Ann. Phys. Chem.*, 1837, [2], 66, 113.

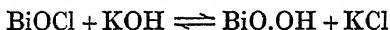
⁹ Jacquelin, *loc. cit.*

other oxidising agents upon bismuth trichloride.¹ (4) It is formed by the action of dilute hydrochloric acid on bismuth trioxide; thus



Colourless tetragonal crystals may be obtained by a suitable modification of this method.² (5) When bismuth sulphate is heated with sodium chloride and the mixture treated with water, bismuthyl chloride remains undissolved.³

Bismuthyl chloride is a white, crystalline powder.⁴ On heating, the colour changes to yellow, and in parts brown, this disappearing only partially on cooling; the colour change thus appears to be partly physical and partly chemical. The compound also darkens on exposure to light.⁵ The crystals belong to the tetragonal system, have a density⁶ of 7.717 at 15° C. and a molecular volume of 33.7; the density of the precipitated form⁷ is 7.2 at 20° C. Melting occurs at red heat without decomposition, and on solidifying a pale yellow, crystalline mass is formed. Prolonged heating at a high temperature causes slight volatilisation, possibly of bismuth trichloride,⁸ although it is also suggested that true sublimation occurs to a slight degree.⁹ The oxychloride is almost insoluble in water¹⁰ and in liquid ammonia.¹¹ It dissolves readily in both hydrochloric and sulphuric acids, with the formation of the trichloride and sulphate respectively; it also dissolves in nitric acid on heating, and from this solution it is re-deposited by evaporation. It reacts with alkalis, especially when the solutions are concentrated.¹² It is probable that with a dilute solution of potassium hydroxide a reversible reaction takes place according to the equation



With concentrated solutions the action is much more complex.¹³ When heated with mercuric oxide it is partially converted to bismuth trioxide.¹⁴ It is reduced to metal by fusion with potassium cyanide, and also by heating in a current of hydrogen; in the latter case some trichloride volatilises.¹⁵

Two hydrates have been reported: the *monohydrate*,¹⁶ $\text{BiOCl.H}_2\text{O}$, and the *trihydrate*, $\text{BiOCl.3H}_2\text{O}$, both of which have been stated to become anhydrous at 100° C.; but from a study of the equilibrium of the system $\text{Bi}_2\text{O}_3\text{--HCl--H}_2\text{O}$ it would appear that no hydrate of bismuthyl chloride can exist at 25° C.; the stable phase which separates out from solutions containing 25 to 33.67 per cent. HCl (up to the

¹ Thomas, *Ann. Chim. Phys.*, 1898, [7], 13, 145; *Compt. rend.*, 1896, 122, 611.

² Muir, *J. Chem. Soc.*, 1881, 39, 36; de Schulten, *Bull. Soc. chim.*, 1900, [3], 23, 156.

³ Lebaigue, *J. Pharm. Chim.*, 1861, [3], 39, 108.

⁴ Heintz, *Pogg. Annalen*, 1844, 63, 72; Ruge, *J. prakt. Chem.*, 1865, 96, 133.

⁵ Herz, *Zeitsch. anorg. Chem.*, 1903, 36, 346.

⁶ de Schulten, *loc. cit.*

⁷ Muir, *J. Chem. Soc.*, 1881, 39, 37.

⁸ Ruge, *loc. cit.*; Arppe, *loc. cit.*

⁹ Herz, *loc. cit.*

¹⁰ Rose, *loc. cit.*

¹¹ Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 827.

¹² Jacquelin, *loc. cit.*; Stromeyer, *Pogg. Annalen*, 1832, 26, 549; Warington, *Phil. Mag. and Annals*, 1831, 9, 30.

¹³ Herz and Muhs, *Zeitsch. anorg. Chem.*, 1904, 39, 115.

¹⁴ Smith and Heyl, *Zeitsch. anorg. Chem.*, 1894, 7, 87.

¹⁵ Rose, *Pogg. Annalen*, 1860, 110, 425.

¹⁶ Heintz, *Pogg. Annalen*, 1844, 63, 55.

point 33.7 per cent. HCl, 58.7 per cent. Bi_2O_3 , 7.6 per cent. H_2O) being anhydrous bismuthyl chloride.¹ (See p. 164.) The solubility product of the monohydrate² is, however, stated to be 1.58×10^{-31} .

The existence of other oxychlorides to which the formulæ $\text{Bi}_2\text{O}_3\text{Cl}_2$, $\text{Bi}_3\text{O}_2\text{Cl}_3$ and $\text{Bi}_4\text{O}_3\text{Cl}_4$ have been ascribed has been suggested from time to time, but it has not been definitely established that these are chemical entities.³ A study of the hydrolytic dissociation of bismuth trichloride indicates that only one oxychloride exists.⁴

From the experimental result shown by the equation



the heat of formation of bismuthyl chloride is calculated to be 88,180 gram-calories.⁵

Bismuth Chlorate.—Bismuth chlorate does not appear to have been isolated, for although bismuth hydroxide dissolves readily in dilute chloric acid, the solution decomposes on concentration.⁶ When a hot aqueous solution of bismuth nitrate and sodium chlorate is cooled, long, glistening prisms of **bismuthyl chlorate**, BiOClO_3 , separate. This substance does not appear to react when warmed with either carbon or a mixture of carbon and sulphur; but it detonates on heating with potassium cyanide.⁷

Bismuth and Bismuthyl Perchlorates.—Muir, in one of his early investigations on bismuth compounds, claimed to have prepared bismuthyl perchlorate, BiOClO_4 , by heating powdered bismuth in a dilute solution of perchloric acid.⁸ The solution of bismuth in perchloric acid is, however, accompanied by the reduction of the acid to chloric acid and the liberation of the explosive chlorine dioxide; hence the experiment can be carried out safely only by employing small quantities of 40 per cent. acid and heating very carefully. A similar product is obtained by dissolving bismuth oxide in the acid. The normal perchlorate can also be obtained by careful employment of the latter method.⁹ In this way the *pentahydrate*, $\text{Bi}(\text{ClO}_4)_3 \cdot 5\text{H}_2\text{O}$, has been obtained in the form of small, hexagonal plates, which are extremely reactive to water, yielding a bismuthyl salt. An unstable *trihydrate* of bismuthyl perchlorate, $\text{BiOClO}_4 \cdot 3\text{H}_2\text{O}$, is obtained by evaporating a solution of bismuth oxide in a more dilute acid, or by adding water to the normal salt and evaporating over calcium chloride; this passes readily into well-formed hygroscopic rhombohedra of the *monohydrate*, $\text{BiOClO}_4 \cdot \text{H}_2\text{O}$, which is the most stable body of this series. By careful drying at 80° to 100°C. , the anhydrous perchlorate is obtained as a white powder. All these oxychlorates are soluble in water, yielding clear solutions, without appreciable hydrolysis.¹⁰ A

¹ Waris, *J. Indian Chem. Soc.*, 1925, 1, 307.

² Feitknecht, *Helv. Chim. Acta*, 1933, 16, 1302.

³ Jaquelain, *loc. cit.*; Dehérain, *Bull. Soc. chim.*, 1862, 4, 23; Muir, *J. Chem. Soc.*, 1877, 32, 133; 1878, 33, 193; 1881, 39, 32; Merz and Weith, *Ber.*, 1880, 13, 210; Thomas, *Compt. rend.*, 1896, 122, 611.

⁴ Dubrisay, *Compt. rend.*, 1909, 149, 122; Herz and Bulla, *Zeitsch. anorg. Chem.*, 1909, 61, 387.

⁵ Thomsen, *Ber.*, 1883, 16, 39.

⁶ Wachter, *Annalen*, 1844, 52, 233.

⁷ Vanino and Musgnug, *Ber.*, 1917, 50, 323.

⁸ Muir, *Chem. News*, 1876, 33, 15.

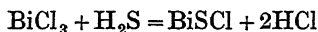
⁹ Fichter and Jenny, *Helv. Chim. Acta*, 1923, 6, 225.

¹⁰ Smith, *J. Amer. Chem. Soc.*, 1923, 45, 360.

basic perchlorate, whose composition approximates to the formula $\text{BiOH} \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$, has been obtained by saturating concentrated perchloric acid with bismuth trioxide.¹

Conductivity measurements on solutions of bismuth perchlorate indicate that a very soluble basic salt, $\text{Bi}(\text{OH})_2\text{ClO}_4$, is stable even in the presence of a moderate excess of perchloric acid, and that it is converted into less basic salts such as $\text{Bi}(\text{OH})(\text{ClO}_4)_2$ or $\text{Bi}(\text{ClO}_4)_3$ only slowly on addition of excess of acid. The first compound has the conductivity of a non-hydrolysed univalent salt² (see p. 146).

Bismuth Thiochloride, BiSCl , was first obtained by Schneider by heating bismuth ammonium chloride either with sulphur or in a current of hydrogen sulphide.³ It has also been obtained by heating bismuth trichloride with sulphur,⁴ by the action of hydrogen sulphide on bismuth trichloride at the ordinary temperature, or at temperatures below red heat,⁵



and by the action of chlorine on bismuth trisulphide at temperatures below red heat :⁶



The thiochloride crystallises in dark grey, metallic needles, which appear ruby-coloured under the microscope. It is decomposed on heating in air, bismuth trichloride and sulphur dioxide volatilising, leaving a residue of oxychloride and basic sulphate; on heating in a current of carbon dioxide, bismuth trichloride volatilises, leaving a residue of bismuth trisulphide; in a current of hydrogen, bismuth trichloride, hydrogen chloride and hydrogen sulphide are volatilised, leaving bismuth contaminated with a little chlorine and sulphur. By strongly heating in a current of hydrogen sulphide it is converted into bismuth trisulphide. It is not attacked by water or dilute mineral acids, even on boiling; but it is decomposed by concentrated acids, hydrogen sulphide being liberated by hydrochloric acid, and sulphur by nitric acid. Potassium hydroxide (and weaker bases more slowly), decomposes it with liberation of chlorine.

Bismuth Selenochloride, BiSeCl , is obtained in the form of small, dark grey, metallic needles by the action of bismuth selenide on molten ammonium bismuth chloride.⁷ It is decomposed into bismuth trichloride and bismuth selenide on heating in a current of carbon dioxide. It is not attacked by water, and hardly at all by concentrated hydrochloric acid; concentrated nitric acid decomposes it with liberation of selenium. Chlorine is liberated by the action of potassium hydroxide, and more slowly by weaker bases.

Bismuth and Bromine.

Bromine combines with bismuth less readily than does chlorine, but if arsenic be present a reaction takes place at the ordinary temperature.⁸

¹ Fichter and Jenny, *loc. cit.*

² Smith, *loc. cit.*

³ Schneider, *Pogg. Annalen*, 1854, 93, 464; *Ann. Phys. Chem.*, 1854, 93, 84.

⁴ Muir, *J. Chem. Soc.*, 1877, 32, 177.

⁵ Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 92. See also Schneider, *loc. cit.*

⁶ Muir and Eagles, *loc. cit.*

⁷ Schneider, *Pogg. Annalen*, 1855, 94, 628.

⁸ Serullas, *Ann. Chim. Phys.*, 1828, [2], 38, 318.

Bismuth Dibromide, BiBr_2 .—The evidence for the existence of this compound is as unsatisfactory as that for the existence of the corresponding chlorine compound. Similar methods have been suggested for its preparation, and it is stated to be a brown, or grey, substance, crystallising in needles.¹ Muir thought it probable that a lower bromide was formed by the reduction of the tribromide by hydrogen, but was unable to isolate the substance owing to its instability.² Attempts to elucidate this problem by means of thermal investigation have also been undertaken.³ Herz and Guttman state that the dibromide is a greyish-black substance with a density of 5.9 and a melting point of 198°C. ; while Marino and Becarelli contend

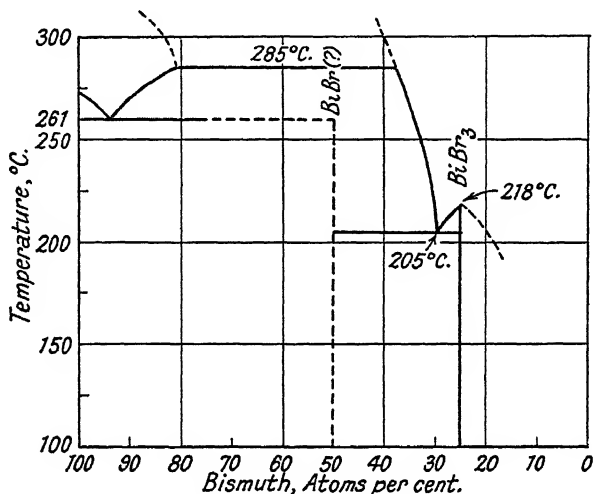


FIG. 6.—Freezing Point Curve of the System Bismuth-Bromine.

that no compound is formed in the system Bi-BiBr_3 , but a series of solid solutions only. The latter investigators find the system similar to that of Bi-BiCl_3 , the solid solution undergoing transformation into first a β -form and then a γ -form, the melting point of the γ -form always being higher than that of either bismuth or bismuth tribromide. On fusion and cooling, the γ -crystals decompose and deposit α -crystals of different composition, and two liquid layers are formed.

Bismuth Tribromide, BiBr_3 , is the only compound of bismuth and bromine indicated on the freezing point curve (fig. 6).⁴ It may be obtained by the direct union of the two elements, an excess of bromine being employed.⁵ A variety of methods has been used by different investigators, the following being some of the more important. Bismuth is heated in bromine vapour;⁶ the two elements are heated

¹ Weber, *Pogg. Annalen*, 1859, 107, 599, 600.

² Muir, *J. Chem. Soc.*, 1876, 29, 145; 1881, 39, 83.

³ Eggink, *Zeitsch. physikal. Chem.*, 1908, 64, 449; Herz and Guttman, *Zeitsch. anorg. Chem.*, 1908, 56, 422; Marino and Becarelli, *Atti R. Accad. Lincei*, 1915, [v], 24, ii, 625; 1916, [v], 25, i, 105.

⁴ *International Critical Tables*, 1928, 4, 23.

⁵ Serullas, *Ann. Chim. Phys.*, 1828, [2], 38, 323; *Pogg. Annalen*, 1828, 14, 113.

⁶ Weber, *Pogg. Annalen*, 1859, 107, 600; Muir, *Chem. News*, 1875, 32, 277.

together in a sealed tube; ¹ powdered bismuth is added to bromine and the mixture allowed to stand for several days, then being distilled and the tribromide purified by repeated distillation; ² or bromine may be dissolved in an organic solvent, such as ether, powdered bismuth added, the mixture filtered after standing for a time, and the solution evaporated *in vacuo*.³

Bismuth tribromide may also be obtained from bismuth trioxide or bismuth trisulphide by heating in bromine vapour. In the former case some oxybromide is also formed, and in the latter some thiobromide.⁴

Bismuth tribromide, by slow distillation, can be obtained in the form of large, flat, golden-yellow crystals.⁵ Its density is 5.604 at 20° C., and its molecular volume at -273° C. (calculated from the density at -194° C. and the coefficient of expansion)⁶ is 77.0. It melts at 218° C., forming a red liquid; the density of the liquid ⁷ between 272° and 330° C. is given by the expression

$$D_4^t = 5.248 - 0.0026t$$

The surface tensions, together with other data for the density,⁸ at various temperatures, are as follows:

Temperature, ° C. .	250	281	299	320	346	370	389	417	442
Density, D_4^t .	4.598	4.525	4.471	4.416	4.348	4.286	4.237	4.164	4.099
Surface Tension (dynes per cm.) .	66.5	63.6	61.6	59.5	56.7	53.8	52.0	48.9	46.2

The boiling point⁹ lies between 454° and 498° C., or 278° C. under a pressure of 11 mm. mercury; ¹⁰ the vapour is deep red in colour.

Bismuth tribromide is not soluble in water but is decomposed by it. It is soluble in both hydrochloric and hydrobromic acids, but it is decomposed by nitric acid. It will also dissolve in alcohol, ether, and to a certain extent in some hydrocarbons, but it is almost insoluble in most other organic solvents.¹¹ It is also said to dissolve in heated arsenic tribromide ¹² and in certain fused metallic halides.¹³

It sublimes in air almost without change, there remaining only a small non-volatile residue, probably of bismuthyl bromide.¹⁴ It absorbs moisture from the air, and is decomposed by excess of water forming

¹ MacIvor, *Chem. News*, 1874, 30, 190.

² Meyer, *Annalen*, 1891, 264, 122.

³ Nicklès, *Compt. rend.*, 1855, 48, 837; *J. prakt. Chem.*, 1859, 79, 14.

⁴ Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 21; Jannarch, *Ber.*, 1891, 24, 3746; *Zeitsch. anorg. Chem.*, 1895, 9, 194.

⁵ Muir, *J. Chem. Soc.*, 1876, 29, 145.

⁶ Biltz, Sapper and Wunnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

⁷ *International Critical Tables*, 1928, 3, 23.

⁸ *International Critical Tables*, 1928, 4, 424; Jaeger and Kahn, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 397; Jaeger, *Zeitsch. anorg. Chem.*, 1917, 101, 16.

⁹ Carnelley and Williams, *J. Chem. Soc.*, 1878, 33, 283. See also Evnevitch and Suchodski, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 1503; Meyer and Krause, *Annalen*, 1891, 264, 124.

¹⁰ Anschütz and Weyer, *Annalen*, 1891, 261, 297.

¹¹ Cavazzi and Tivoli, *Gazzetta*, 1891, 21, ii, 306; Nicklès, *loc. cit.*

¹² Retgers, *Zeitsch. physikal. Chem.*, 1893, 11, 340.

¹³ Isbekov, *Zeitsch. physikal. Chem.*, 1925, 116, 304; *Zeitsch. anorg. Chem.*, 1930, 185, 324.

¹⁴ Thomas, *Compt. rend.*, 1896, 122, 1060; Muir, *J. Chem. Soc.*, 1876, 30, 12; 1877, 32, 137.

bismuthyl bromide. Variation of temperature appears to have but little effect upon the hydrolysis of bismuth tribromide, and only one oxybromide is produced.¹

Nitrogen tetroxide reacts even at the ordinary temperature, producing bismuth oxybromide.² The tribromide forms a number of *ammoniates*, among them being an olive-green compound, $\text{BiBr}_3 \cdot 2\text{NH}_3$, and a light, straw-coloured, amorphous powder, $\text{BiBr}_3 \cdot 3\text{NH}_3$, both of which are decomposed by water, probably with formation of oxybromide. A third compound, $2\text{BiBr}_3 \cdot 5\text{NH}_3$, is said to be formed as a greyish-green sublimate by the action of dry ammonia upon heated bismuth oxybromide; it is not deliquescent, nor is it decomposed by water. All these compounds react readily with hydrochloric acid, forming double salts of bismuth bromide and ammonium chloride: $\text{BiBr}_3 \cdot 2\text{NH}_4\text{Cl} \cdot 3\text{H}_2\text{O}$, $\text{BiBr}_3 \cdot 3\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$, and $2\text{BiBr}_3 \cdot 5\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$. In addition, an ash-grey, crystalline substance has been obtained which is stated to have the composition BiN_2Br_3 .³

When an ether solution of bismuth tribromide is gradually added to dry phosphine, a lustrous, black substance is formed which probably has the composition $\text{PBrH}(\text{BiBr}_2)_3$ or $2\text{BiBr}_3 \cdot \text{HBr} \cdot \text{BiP}$:



It is hygroscopic, and is decomposed by water with liberation of bismuth and formation of phosphine, hydrobromic and phosphoric acids. It is decomposed by a solution of potassium hydroxide with evolution of hydrogen and phosphine, and formation of potassium bromide and phosphate. Concentrated sulphuric acid attacks it only when heated, but concentrated nitric acid acts upon it very violently. It decomposes with violence when heated in air, yielding bromine, bismuth bromide and phosphorus pentoxide, but is stable when heated to 220°C . in a current of carbon dioxide.⁴

Bismuth tribromide does not react readily with sulphur; on heating, only a small quantity of thiobromide, BiSBr , is obtained.⁵ It reacts with hydrogen sulphide at the ordinary temperature; at moderate temperatures bismuth thiobromide, BiSBr , and at higher temperatures bismuth trisulphide, Bi_2S_3 , is formed.⁶ The tribromide is not altered by heating with sulphur dioxide.

The decomposition potential of bismuth tribromide in solution in fused zinc chloride⁷ is 0.46 volt. This places bismuth below mercury in the electrochemical series.

Double and Complex Salts.—If a saturated solution of bismuth tribromide in concentrated hydrobromic acid is cooled to -10°C ., a complex substance of an acidic nature separates out as yellow needles. Its composition is $\text{BiBr}_3 \cdot 2\text{HBr} \cdot 4\text{H}_2\text{O}$ or $\text{H}_2\text{BiBr}_5 \cdot 4\text{H}_2\text{O}$. It is extremely deliquescent and unstable, losing hydrogen bromide when exposed to air.⁸

¹ Dubrisay, *Compt. rend.*, 1909, 149, 122; Herz and Bulla, *Zeitsch. anorg. Chem.*, 1909, 61, 387; 1909, 63, 59.

² Thomas, *loc. cit.*

³ Muir, *J. Chem. Soc.*, 1876, 29, 48; 1876, 30, 14; 1877, 31, 27. See also Field, *J. Chem. Soc.*, 1893, 63, 547; *Chem. News*, 1893, 67, 157.

⁴ Cavazzi and Tivoli, *Gazzetta*, 1891, 21, ii, 306.

⁵ Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 35.

⁶ Muir and Eagles, *Chem. News*, 1895, 71, 35.

⁷ Isbekov, *Zeitsch. anorg. Chem.*, 1930, 185, 324.

⁸ Aloy and Frébault, *Bull. Soc. chim.*, 1906, [3], 35, 396.

Two organic compounds¹ have also been obtained, with the compositions $\text{H}_2\text{BiBr}_5 \cdot 4\text{O}(\text{C}_2\text{H}_5)_2$ and $\text{H}_2\text{BiBr}_5 \cdot 10\text{O}(\text{C}_2\text{H}_5)_2$; both are hygroscopic and unstable. The *alkali salts*, Li_3BiBr_5 , Na_3BiBr_5 and K_3BiBr_5 , and the *thallium salt*, Tl_3BiBr_5 (the latter forming lemon-yellow crystalline plates),² have been isolated. In addition, the *ammonium salt*, $(\text{NH}_4)_2\text{BiBr}_5 \cdot 2\text{H}_2\text{O}$, has been obtained by heating bismuth bromide and ammonium bromide with alcohol and a little ammonium acetate in a sealed tube;³ it is a greenish-yellow, transparent substance, crystallising in the rhombic system and isomorphous with the corresponding chloride and with the double chloride of potassium and bismuth. It loses combined water completely when heated to 100°C .; it is dissociated when strongly heated, and is decomposed by water forming bismuthyl bromide. Several mixed halides of similar composition have also been reported, among them being $\text{K}_2\text{BiClBr}_4$,⁴ $\text{K}_2\text{BiCl}_3\text{Br}_2$,⁵ $\text{K}_2\text{BiCl}_4\text{Br}$,⁶ and $(\text{NH}_4)_2\text{Bi}(\text{Cl}, \text{Br})_3\text{Br}_2$.⁷ Evidence for the existence of a complex of the type H_2BiBr_5 is also obtained from a study of the absorption spectrum of a solution of bismuth tribromide in hydrobromic acid.⁸

An ammonium compound, $\text{NH}_4\text{BiBr}_4 \cdot \text{H}_2\text{O}$, which corresponds to the hypothetical complex acid HBiBr_4 , has also been obtained by the action of bromine on bismuth in alcohol in the presence of ammonium bromide.⁹ It forms yellow, needle-like crystals of the rhombic system, soluble in alcohol, but decomposed by water. From thermal analysis there is evidence for the existence of the aluminium compound¹⁰ AlBiBr_6 , but this substance does not appear to have been isolated. A very complex triple salt, $\text{Rb}_5\text{Au}_2\text{BiBr}_{14}$ or $5\text{RbBr} \cdot 2\text{AuBr}_3 \cdot \text{BiBr}_3$, has been prepared,¹¹ in which the gold is present in the trivalent form. It is a black substance, soluble in hydrobromic acid. It is also possible that complex compounds of bismuth and bromine of the type $\text{K}_2\text{Bi}_3\text{Br}_{11}$, etc., similar to the corresponding compounds of antimony (see p. 77) may exist, but they have not yet been isolated.¹²

Bismuth Oxybromide, or *Bismuthyl Bromide*, BiOBr , can be obtained by the action of water on a solution of bismuth tribromide in hydrobromic acid; it is also believed to be formed by heating together bismuth tribromide and bismuth trioxide.¹³ By a suitable modification of the former method, the crystalline oxybromide may be obtained.¹⁴ The precipitated substance is obtained as a snow-white, amorphous powder of density (at 20°C .)¹⁵ 6.7. The crystalline form is colourless and transparent, density (at 15°C .) 8.082. It melts at a bright red heat, at which temperature bismuth tribromide volatilises; it darkens

¹ Schäfer and Hein, *Zeitsch. anorg. Chem.*, 1917, 100, 249.

² Canneri and Perina, *Gazzetta*, 1922, 52, I, 231.

³ Nicklès, *J. Pharm. Chim.*, 1861, [3], 39, 118; Groth, *Chem. Kryst.*, 1906, I, 431.

⁴ Field, *J. Chem. Soc.*, 1893, 63, 546.

⁵ Atkinson, *J. Chem. Soc.*, 1883, 43, 292.

⁶ Field, *loc. cit.*

⁷ Nicklès, *J. Pharm. Chim.*, 1861, [3], 40, 191.

⁸ Schäfer and Hein, *loc. cit.*

⁹ Nicklès, *Compt. rend.*, 1860, 51, 1097.

¹⁰ Isbekov, *Zeitsch. anorg. Chem.*, 1925, 143, 80.

¹¹ Burkser, Rublov and Sharnovski, *Zeitsch. anorg. Chem.*, 1929, 185, 144.

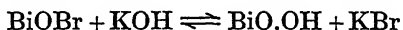
¹² Vournazos, *Zeitsch. anorg. Chem.*, 1930, 112, 369; *Praktika (Akad. Athenon)*, 1932, 7, 227.

¹³ Muir, *J. Chem. Soc.*, 1877, 31, 27.

¹⁴ de Schulten, *Bull. Soc. chim.*, 1900, [3], 23, 157.

¹⁵ Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 37.

on exposure to light ;¹ it is insoluble in water, but dissolves in moderately dilute hydrobromic acid ; it is decomposed by potassium hydroxide as follows :²

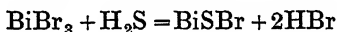


Two other oxybromides have been reported, namely, $\text{Bi}_8\text{O}_{15}\text{Br}_6$ and $\text{Bi}_{11}\text{O}_{13}\text{Br}_7$ (or $7\text{BiOBr} \cdot 2\text{Bi}_2\text{O}_3$), but their identities have not been confirmed.³

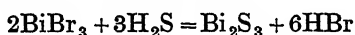
Bismuth oxybromides are partially reduced to metal when heated to a dull red heat in a current of dry ammonia (see also p. 173).

A basic salt, **bismuth oxybromate**, or *bismuthyl bromate*, BiOBrO_3 , has been obtained (mixed with some bismuthyl hydroxide, BiO.OH) by the prolonged action of an aqueous solution of bromic acid upon bismuth hydroxide. The mixture is a white, amorphous, insoluble powder which loses water between 150° and 200° C. and decomposes violently when strongly heated, leaving a residue of bismuth oxybromide. At the same time there is formed a soluble product, the solution of which decomposes on evaporation, with evolution of bromine, while the small amount of residue which is obtained decomposes at once in the air.⁴

Bismuth Thiobromide, BiSBr , has been obtained by heating together a mixture of bismuth tribromide and sulphur.⁵ It may be obtained more readily by the action of hydrogen sulphide on bismuth tribromide, or by the action of bromine upon dried, precipitated bismuth trisulphide. In each case the action must be carefully regulated. The former reaction, when carried out at temperatures up to a very low red heat, may be represented by the equation⁶



while at full red heat the following occurs :



The second reaction is carried out at a low red heat, and may be represented by the equation



Bismuth and Iodine.

Bismuth Diiodide.—As with other bivalent compounds of bismuth, the question of the diiodide has given rise to much discussion. An early attempt was made to prepare this substance by melting together bismuth triiodide and bismuth, but the results were inconclusive.⁷ Later, the thermal investigation of the system bismuth triiodide–bismuth appeared to afford evidence of the existence of the compound BiI_2 , which crystallised with metallic lustre, had a density

¹ Herz, *Zeitsch. anorg. Chem.*, 1903, 36, 346.

² Herz and Muhs, *Zeitsch. anorg. Chem.*, 1904, 39, 115.

³ Muir, *J. Chem. Soc.*, 1876, 30, 12; 1877, 31, 27; 1877, 32, 137; 1881, 39, 22. See also Thomas, *Compt. rend.*, 1896, 122, 1060.

⁴ Rammelsberg, *Pogg. Annalen*, 1842, 55, 76.

⁵ Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 33.

⁶ Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 90.

⁷ Weber, *Pogg. Annalen*, 1859, 107, 601.

of 6.5, and decomposed below its melting point.¹ A study of the system bismuth-iodine (fig. 7) by thermal analysis, however, failed to yield evidence for any compound other than the triiodide.² More recently, a similar investigation, while providing no evidence of the existence of bismuth diiodide, indicated a reaction at 281° C. which

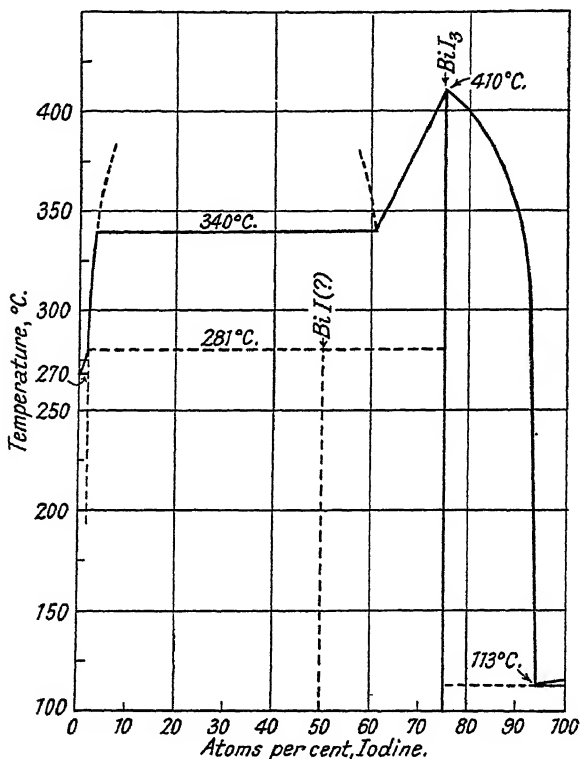


FIG. 7.—Freezing Point Curve of the System Bismuth-Iodine.

was attributed to the formation of a compound, BiI , from bismuth triiodide and liquid.³

Bismuth diiodide is said to be obtained by distilling methyl iodide through bismuth monoxide.⁴ The monoxide is prepared by the method of Tanatar (see p. 183),⁵ and the distillation is carried out in stages, at a maximum temperature of 262° C., the monoxide being maintained at the same maximum temperature at each stage; between each stage the apparatus is cooled down to the ordinary temperature.⁶ Three products are obtained:

(1) A non-volatile, brick-red homogeneous powder which remains in the reaction vessel. This substance, **bismuth suboxyiodide**,

¹ Herz and Guttman, *Zeitsch. anorg. Chem.*, 1908, 56, 422.

² Marino and Becarelli, *Atti R. Accad. Lincei*, 1912, [v], 21, 695.

³ van Klooster, *Zeitsch. anorg. Chem.*, 1913, 80, 104.

⁴ Denham, *J. Amer. Chem. Soc.*, 1921, 43, 2367.

⁵ Tanatar, *Zeitsch. anorg. Chem.*, 1901, 27, 437.

⁶ For description of apparatus, see Denham, *J. Chem. Soc.*, 1917, III, 32.

$2\text{BiI}_2 \cdot 3\text{BiO}$, is stable in air, non-volatile at 300°C . but decomposed above 350°C . probably into bismuth and bismuth oxyiodide. A saturated aqueous solution of this substance, after filtration, reacts only very faintly with both hydrogen sulphide and silver nitrate, but the substance is decomposed into bismuth and the trivalent salt by sulphuric acid, acetic acid, hydrochloric acid and sodium hydroxide. It is insoluble both in alcohol and in an aqueous solution of potassium iodide. It is a reducing agent, reducing an acid solution of potassium permanganate. The identity of this compound and its distinction from bismuth oxyiodide, BiOI , have been confirmed by comparing the conductivities of its solutions with those of the oxyiodide; the resistance of the latter was 745 ± 15 ohms and that of the former 9000 ± 900 ohms.

(2) A red, volatile product which condenses in the cool part of the apparatus. It is claimed that this substance is bismuth diiodide, BiI_2 . It crystallises in bright red, long needles, of the rhombic system. Its solution in water, free from oxygen, yields much stronger reactions for bismuth ion and iodide ion than the afore-mentioned suboxyiodide. In the absence of oxygen it dissolves in alcohol and in methyl iodide, forming in both cases a clear yellow liquid; it dissolves readily in an aqueous solution of potassium iodide. It is a reducing agent, rapidly reducing a solution of iodine, and an acid solution of potassium permanganate; it decomposes above 400°C . into bismuth triiodide, which volatilises, leaving a residue of bismuth.

(3) The distillate, a pale yellow liquid, is considered to contain a mixture of bismuth diiodide and bismuth dimethyl, $\text{Bi}(\text{CH}_3)_2$; the evidence for this is inconclusive, but the distillate oxidises readily, producing a strongly reducing substance which is thought to be dimethoxybismuth, $\text{Bi}(\text{OCH}_3)_2$.

In connection with this preparation, however, it must be remembered that the evidence for the existence of bismuth monoxide itself has been criticised.¹

X-ray examination has failed to reveal the existence of a lower iodide than bismuth triiodide.² This evidence is, however, not conclusive.

Bismuth Triiodide, BiI_3 , was probably first prepared by Berthémot by synthesis from the elements;³ this synthesis has since been effected in a variety of ways.⁴ Owing to the small reactivity of the elements, however, combination is effected only with difficulty. The iodide may be purified by sublimation in a slow current of hydrogen.

It may also be obtained by precipitation from a solution of a bismuth salt in acetic acid with potassium iodide,⁵ by the action of concentrated hydriodic acid on bismuth trioxide at the ordinary temperature,⁶ or on bismuth oxychloride,⁷



¹ Neusser, *Zeitsch. anorg. Chem.*, 1924, 135, 313; 1924, 138, 180.

² Caglioti, *Gazzetta*, 1930, 60, 933.

³ Berthémot, *J. Pharm.*, 1828, 14, 616.

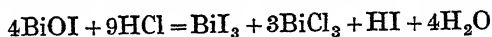
⁴ Rammelsberg, *Pogg. Annalen*, 1839, 48, 166; Heintz, *ibid.*, 1844, 63, 75; Weber, *ibid.*, 1859, 107, 600; Nicklès, *Compt. rend.*, 1860, 50, 872; Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 33; Schneider, *J. prakt. Chem.*, 1894, [2], 50, 463.

⁵ Rammelsberg, *loc. cit.*; Arppe, *Pogg. Annalen*, 1845, 64, 248; Gott and Muir, *J. Chem. Soc.*, 1888, 53, 137.

⁶ Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 36.

⁷ Rammelsberg, *loc. cit.*; Muir, Hoffmeister and Robbs, *loc. cit.*

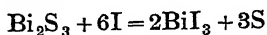
or by the action of hydrochloric acid on bismuth oxyiodide,¹



or



When a mixture of bismuth trisulphide and iodine is heated, bismuth triiodide sublimes, leaving a residue of bismuth thioiodide;² according to another authority, bismuth triiodide and sulphur only are produced³ in accordance with the reaction



Bismuth triiodide is also formed by the action of ethyl iodide on bismuth trichloride in the presence of ethyl chloride.⁴

Crystalline bismuth triiodide may be obtained by saturating a solution of Bettendorff's reagent (a solution of stannous chloride in hydrochloric acid) with iodine and adding a solution of bismuth trioxide or bismuth oxychloride in hydrochloric acid.⁵ The size of the crystals depends on the concentration of the solution; they can be purified by drying and heating carefully in an evacuated tube to below the melting point, finally subliming in carbon dioxide or hydrogen.

Bismuth triiodide crystallises in the hexagonal system :

$$a = 7.498 \text{ \AA.}, \quad c = 20.676 \text{ \AA.}$$

The unit cell contains six molecules.⁶ Its colour is variously described as dark green, black and grey-black; in the powdered form it is dark brown. Its density,⁷ D_4^{20} , is 5.7, and the molecular volume at -273°C. , calculated from the density at -194°C. and the coefficient of expansion,⁸ is 98.6. Its melting point⁹ is 410° to 439°C. It volatilises at slightly higher temperatures, forming a red-brown vapour. It sublimes unchanged when heated in an atmosphere of carbon dioxide or hydrogen, but evidence of thermal dissociation has been obtained spectroscopically.¹⁰

It is stable in air, but volatilises with partial decomposition when heated in air, leaving a non-volatile residue of oxyiodide or trioxide.¹¹ It is not hygroscopic, but is decomposed by water.

It is soluble in hydrochloric acid and in hydriodic acid, slightly soluble in absolute alcohol, and more soluble in benzene, toluene and xylene. It is also soluble in arsenic tribromide.¹² The solubility in organic solvents is greatly increased by the presence of arsenic tribromide.¹³

¹ Muir, *J. Chem. Soc.*, 1878, 33, 201; Muir, Hoffmeister and Robbs, *loc. cit.*

² Schneider, *Pogg. Annalen*, 1854, 93, 64; 1856, 99, 470; 1860, 110, 147.

³ Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 92.

⁴ Auger, *Compt. rend.*, 1904, 139, 671.

⁵ Birekenbach, *Ber.*, 1907, 40, 1404.

⁶ Braekken, *Zeitsch. Krist.*, 1930, 74, 67. See also Linck, *Ber.*, 1907, 40, 1405; Retgers, *Zeitsch. anorg. Chem.*, 1893, 3, 345; Nicklès, *loc. cit.*; Schneider, *J. prakt. Chem.*, 1860, 79, 421.

⁷ *International Critical Tables*, 1926, 1, 111.

⁸ Biltz, Sapper and Wunnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

⁹ *International Critical Tables*, 1926, 1, 111; Carnelley and Williams, *J. Chem. Soc.*, 1880, 37, 125.

¹⁰ Neumin, *Physikal. Zeitsch. Sowjet-union*, 1932, 2, 422.

¹¹ Thomas, *Compt. rend.*, 1896, 123, 1060; Muir, Hoffmeister and Robbs, *loc. cit.*

¹² Retgers, *Zeitsch. anorg. Chem.*, 1893, 3, 345; *Zeitsch. physikal. Chem.*, 1893, 11, 340.

¹³ Nicklès, *loc. cit.*

Bismuth triiodide is hydrolysed slowly by cold water, slightly more rapidly by hot water.¹ The rate of hydrolysis, however, at 25° C. and at 50° C. is so slow that the conditions of equilibrium have not been determined.² Two products of hydrolysis have been described:³ a black compound, which is formed when water is first added to the triiodide, and a brick-red substance which is obtained when the concentration of bismuth in the liquid phase falls below 0.002 gram-atom per litre and which has the composition of bismuth oxyiodide, BiOI. The black substance has not been obtained pure, but analysis indicates a composition corresponding to $\text{Bi}_2\text{O}_3 \cdot 5\text{HI}$ or $2\text{BiOI} \cdot 3\text{HI} \cdot \text{H}_2\text{O}$.

Bismuth triiodide does not appear to react with hydrogen sulphide when heated in a current of that gas.⁴

When the triiodide is heated with dry ammonia, a brick-red compound, $\text{BiI}_3 \cdot 3\text{NH}_3$, is formed. This substance is decomposed by water with the separation of ammonium iodide.⁵

Bismuth triiodide is decomposed by nitric acid, with the liberation of iodine. Muir stated that it reacted on heating with nitrogen peroxide and was partially converted into oxyiodide; this action was, however, much less complete than the corresponding reaction with either bismuth trichloride or tribromide. It has since been shown that at the ordinary temperature the triiodide is converted to trioxide by reaction with nitrogen peroxide, no oxyiodide being formed unless air is present.⁶

By reaction with caustic alkalis (and less readily with alkali carbonates) it is converted to trioxide, admixed with a little bismuth iodate. The reaction proceeds by stages. Taking the action of a solution of potassium hydroxide as typical, when the concentration of the alkali is less than 0.375 mole per litre the main product is the oxyiodide, BiOI. When the concentration is greater than this, this oxyiodide by a further reaction is transformed into the white compound $\text{BiOI} \cdot 2\text{Bi}_2\text{O}_3$; with excess of alkali the main product is bismuth trioxide.⁷ The triiodide reacts with alkali sulphides to form bismuth trisulphide. When heated with excess of mercuric oxide, or of mercuric sulphide, it is converted to the trioxide or the trisulphide, respectively.

The molecular weight of bismuth triiodide,⁸ as determined from a solution in fenchone, is in accordance with the formula BiI_3 .

The triiodide resembles the trichloride and the tribromide in forming a number of complex compounds and double salts. An iodobismuthous acid, $\text{HBiI}_4 \cdot x\text{H}_2\text{O}$ or $\text{BiI}_3 \cdot \text{HI} \cdot x\text{H}_2\text{O}$ (where $x = 3$ or 4), is reported to have been obtained in the form of rhombic, pyramidal crystals from a solution of the triiodide in concentrated hydriodic acid by evaporation over sulphuric acid.⁹ This dissolves in a solution of potassium iodide, but is decomposed by water forming bismuth oxyiodide.

An examination of cerebrospinal fluid and brain containing bismuth

¹ Gott and Muir, *loc. cit.*

² Herz and Bulla, *Zeitsch. anorg. Chem.*, 1909, 61, 387; 63, 59.

³ Dubrisay, *Compt. rend.*, 1909, 149, 451.

⁴ Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 90.

⁵ Rammelsberg, *Pogg. Annalen*, 1839, 48, 168.

⁶ Thomas, *Compt. rend.*, 1896, 123, 1060; Muir, *J. Chem. Soc.*, 1878, 33, 200; Heintz, *Pogg. Annalen*, 1844, 63, 75.

⁷ Montignie, *Bull. Soc. chim.*, 1934, [5], 1, 692; François and Delwaulle, *ibid.*, 1933, [4], 53, 1104.

⁸ Rimini and Olivari, *Atti R. Accad. Lincei*, 1907, [5], 16, I, 665.

⁹ Arppe, *Pogg. Annalen*, 1845, 64, 250.

indicated that the bismuth was present in the anion.¹ From a study of ionic migration in the compound Na_2BiI_5 it is found that the bismuth occurs in the complex anion BiI_5^- . Compounds of the form RBiI_4 and R_3BiI_6 , in which R represents an organic radical, have been obtained.²

Among inorganic complex or double salts which have been reported are the following :

The *sodium salt* $\text{NaBiI}_4 \cdot \text{H}_2\text{O}$, prepared by the action of iodine on bismuth in a saturated solution of sodium chloride; it forms brownish-black crystals belonging to the monoclinic system:³ $a:b:c = 0.864:1:0.717$; $\beta = 102^\circ 21'$. $\text{Na}_2\text{BiI}_5 \cdot 4\text{H}_2\text{O}$, prepared by the action of anhydrous sodium iodide upon bismuth chloride in ethyl acetate;⁴ it has a density of 3.33, melts at 93° to 94° C. and is soluble in water and various organic solvents, but undergoes hydrolysis with excess of the former solvent. $\text{Na}_3\text{Bi}_2\text{I}_9 \cdot 12\text{H}_2\text{O}$, which separates out from a concentrated solution of sodium iodide saturated with bismuth triiodide.⁵

Numerous *potassium double salts* have been reported, including⁶ $\text{KI} \cdot 2\text{BiI}_3$, $\text{KI} \cdot \text{BiI}_3 \cdot \text{H}_2\text{O}$, $2\text{KI} \cdot \text{BiI}_3$, $2\text{KI} \cdot \text{BiI}_3 \cdot 4\text{H}_2\text{O}$, $3\text{KI} \cdot \text{BiI}_3$, $3\text{KI} \cdot 2\text{BiI}_3 \cdot 2\text{H}_2\text{O}$, $4\text{KI} \cdot \text{BiI}_3$, $4\text{KI} \cdot \text{BiI}_3 \cdot \text{HI}$, $4\text{KI} \cdot 2\text{BiI}_3$ and $6\text{KI} \cdot 2\text{BiI}_3$. Investigation of the condition of equilibrium at 15° , 35° and 55° C. within the system BiI_3 - KI - H_2O revealed the existence⁷ of two compounds only, $\text{KI} \cdot \text{BiI}_3 \cdot \text{H}_2\text{O}$ or $\text{KBiI}_4 \cdot \text{H}_2\text{O}$ and $2\text{KI} \cdot \text{BiI}_3 \cdot \text{H}_2\text{O}$ or $\text{K}_2\text{BiI}_5 \cdot \text{H}_2\text{O}$; the former of these crystallises as bright red monoclinic prisms and the latter as deep red flat quadratic prisms with pyramidal ends. Both compounds can be dehydrated by treatment *in vacuo* over sulphuric acid.

The *cæsium salt*,⁸ $\text{Cs}_3\text{Bi}_2\text{I}_9$, is prepared by the action of a solution of bismuth hydroxide, bismuthyl carbonate or bismuth oxyiodide in hydriodic acid upon cæsium nitrate, or by the interaction of cæsium iodide with bismuth triiodide. It forms hexagonal crystals, hydrolysed slowly in cold water, rapidly in hot water. It is fairly stable when heated and its use has been suggested for the quantitative determination of cæsium.

Somewhat similar compounds of *barium*, *calcium*, *magnesium*, *beryllium* and *aluminium* have also been reported.⁹

Most of the foregoing compounds form red or dark red crystals; they are all hydrolysed by water, yielding bismuthyl iodide.¹⁰

Two *ammonium compounds* have also been obtained and examined. The salt $\text{NH}_4\text{BiI}_4 \cdot \text{H}_2\text{O}$ is obtained as a precipitate when iodine reacts on bismuth in a concentrated aqueous solution of ammonium iodide;

¹ Gurchot, Hanzlik and Spaulding, *J. Pharmacol.*, 1932, 45, 427.

² Bartholomew and Burrows, *J. Proc. Roy. Soc. New South Wales*, 1926, 60, 608. For other compounds with organic bases, see Kraut, *Annalen*, 1881, 210, 310; Jörgensen, *Jahresber.*, 1869, 717.

³ Nicklès, *J. Pharm. Chim.*, 1861, [3], 40, 321; Groth, *Chem. Kryst.*, 1906, I, 440.

⁴ Gurchot, Hanzlik and Spaulding, *loc. cit.* See also Nicklès, *J. Pharm. Chim.*, 1861, [3], 40, 324; 1862, [3], 41, 148; *Compt. rend.*, 1860, 50, 872; Dragendorff, *Pharm. Zeit.*, 1866, 5, 82; Astre, *Compt. rend.*, 1890, 110, 525, 1137; Jurist and Christiansen, *J. Amer. Pharm. Soc.*, 1934, 23, 15.

⁵ Arppe and Linau, *Pogg. Annalen*, 1860, 111, 241.

⁶ Motard, *Compt. rend.*, 1934, 198, 655; Astre, *ibid.*, 1890, 110, 525; Astre, *ibid.*, p. 1137; Arppe and Linau, *loc. cit.*; Arppe, *Pogg. Annalen*, 1845, 64, 250.

⁷ Delwaule, *Compt. rend.*, 1934, 199, 948.

⁸ Meloche and Clark, *J. Amer. Chem. Soc.*, 1930, 52, 907; Wells and Foote, *Amer. Chem. J.*, 1897, [4], 3, 461.

⁹ Welkow, *Ber.*, 1874, 7, 804. ¹⁰ See also Canneri and Perina, *Gazzetta*, 1922, 52, I, 231.

it may also be obtained by the action of iodine on bismuth in alcohol in the presence of ammonium iodide.¹ It forms black, needle-shaped crystals of the rhombic system. Another compound, $(\text{NH}_4)_4\text{BiI}_7 \cdot 3\text{H}_2\text{O}$, is obtained when a warm, concentrated solution of ammonium iodide is saturated with bismuth triiodide. On evaporation, large, dark reddish-brown, rectangular prismatic crystals separate. They appear to be isomorphous with the corresponding double salt of antimony; they are hygroscopic and are decomposed by water.²

A solution made by adding excess of a solution of potassium iodide to a solution of bismuth nitrate is known as *Dragendorff's reagent*. It contains a complex iodide of bismuth and potassium and is used in testing for alkaloids.³

Complex compounds of bismuth iodide and organic bases have also been described.⁴

Bismuth Oxyiodide, or *Bismuthyl Iodide*, BiOI , is most readily obtained by the hydrolysis of bismuth triiodide. Various other methods for its preparation have been described, including the oxidation of bismuth triiodide, the action of heat upon a mixture of bismuth triiodide and bismuth trioxide, or the direct combination of those compounds in a solution of potassium iodide at the ordinary temperature,⁵ and the distillation of methyl iodide through bismuth trioxide.⁶

It is a red, crystalline powder; the crystals are variously described as brick-red, cubic microcrystals,⁷ or as copper-red, rhombic leaflets.⁸ The density⁹ at 15°C . is 7.922.

The oxyiodide is stable in air, melting at red heat without decomposition. When heated in the absence of air it sublimes with partial decomposition, and when more strongly heated it is converted to bismuth trioxide. It is only slightly attacked by water, but readily by dilute mineral acids with the formation of bismuth triiodide. It dissolves in concentrated hydrochloric acid, forming a yellow solution. It is decomposed by both concentrated sulphuric acid and concentrated nitric acid with evolution of iodine. It is not attacked to any appreciable extent by dilute alkaline solutions, even on warming; but it is converted to trioxide by the action of a concentrated solution of potassium hydroxide. It is not attacked by a solution of potassium chloride. It is completely converted into trisulphide by the action of a mixture of potassium hydroxide and ammonium sulphide.

Various other oxyiodides have been reported from time to time, but their existence has not been confirmed (see also p. 179).¹⁰

Bismuth Iodate.—Normal bismuthiodate, $\text{Bi}(\text{IO}_3)_3$, can be obtained as a white powder, insoluble in water and acetic acid, by treating a solution of bismuth acetate with iodic acid;¹¹ in the presence of acetic acid the precipitation is quantitative.

¹ Nicklès, *Compt. rend.*, 1860, 51, 1097; *J. Pharm. Chim.*, 1861, [3], 40, 322.

² Linau, *Pogg. Annalen*, 1860, 111, 242.

³ Dragendorff, "*Plant Analysis*" (London, 1884), p. 54; Mangini, *Gazzetta*, 1882, 12, 155; Thresh, *Pharm. J.*, 1880, (3), 10, 641, 809; Yvon, *ibid.*, 1874, [3], 4, 1014.

⁴ Vanino and Hauser, *Ber.*, 1902, 35, 663.

⁵ François and Delwaulle, *Compt. rend.*, 1933, 196, 1731.

⁶ Denham, *J. Amer. Chem. Soc.*, 1921, 43, 2367.

⁷ Fischer, "*Die neuen Arzneimittel*," 1893, p. 25.

⁸ Schneider, *J. prakt. Chem.*, 1860, 79, 424.

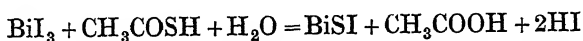
⁹ de Schulten, *Bull. Soc. chim.*, 1900, [3], 23, 156.

¹⁰ Blythe, *Chem. News*, 1896, 74, 200.

¹¹ Buisson and Ferray, *Zeitsch. anal. Chem.*, 1874, 13, 61.

When iodic acid and potassium iodate are added to a solution of bismuth nitrate, a white precipitate is produced.¹ A white precipitate is also obtained by precipitating basic bismuth nitrate from a solution of the normal salt and treating the filtrate from this with sodium iodate. The white powder obtained can be dried at 100° C. and is stated to be insoluble in both nitric acid and water. On heating it loses both oxygen and iodine, leaving a residue which is probably bismuth oxyiodide.²

Bismuth Thioiodide, BiSI, is obtained by dissolution of bismuth trisulphide in molten bismuth triiodide,³ by heating together bismuth trisulphide and iodine,⁴ by heating together bismuth trisulphide, iodine and sulphur for a long time,⁵ or by the action of thioacetic acid on bismuth triiodide in the cold :⁶



It crystallises in small, steel-grey, metallic needles resembling bismuth glance. It is decomposed on heating to the melting point into bismuth trisulphide and triiodide. It is not acted upon by water or dilute mineral acids even on boiling; concentrated hydrochloric acid decomposes it with evolution of hydrogen sulphide, concentrated nitric acid with evolution of iodine and sulphur, iodine also being liberated by the action of warm potassium hydroxide (ammonia and other weak bases act in a similar manner, but more slowly and less completely).

BISMUTH AND OXYGEN.

Several oxides of bismuth have been reported: they include, bismuth monoxide, BiO, trioxide, Bi₂O₃, tetroxide (or dioxide), Bi₂O₄, pentoxide, Bi₂O₅, and hexoxide, Bi₂O₆. The most stable of these is the trioxide, which is mainly basic in its reactions, possessing only very feeble acidic properties. Bismuth monoxide is stated to be weakly basic, and halide salts derived from this oxide have been reported (pp. 158, 171, 175). The higher oxides are unstable and very slightly acidic; alkali bismuthates, derived from the pentoxide, are however more stable, and are employed as oxidising agents.

Bismuth Monoxide, BiO.—Various methods for the preparation of bismuth monoxide were described by early investigators, who frequently referred to it as a suboxide, but in most cases the product was either impure or later proved to be a mixture of bismuth and its trioxide. It is probable that the monoxide was first obtained in a fairly pure condition by dissolving equivalent proportions of bismuth trioxide and stannous chloride in hydrochloric acid, pouring the mixture into a moderately concentrated solution of potassium hydroxide, filtering and washing the precipitate with a cold solution of potassium hydroxide. The product should be dried in a vacuum over sulphuric acid.⁷

¹ Pleischl, *Schweigger's J.*, 1838, 15, 1.

² Rammelsberg, *Pogg. Annalen*, 1838, 44, 568.

³ Schneider, *Pogg. Annalen*, 1860, 110, 147; *J. prakt. Chem.*, 1860, 79, 422; Muir and Eagles, *J. Chem. Soc.*, 1895, 67, 92.

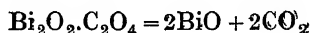
⁴ Schneider, *loc. cit.*

⁵ Linau, *Pogg. Annalen*, 1860, 110, 148.

⁶ Tarugi, *Gazzetta*, 1897, 27, I, 316.

⁷ Schneider, *Pogg. Annalen*, 1844, 63, 53; 1846, 68, 49; 1853, 88, 45. See also Muir, *J. Chem. Soc.*, 1877, 31, 650; 32, 128; Berzelius, "*Lehrbuch*" (Dresden, 1826), 2, 273; Thomson, *Proc. Roy. Phil. Soc. Glasgow*, 1842, 1, 4; Heintz, *Pogg. Annalen*, 1844, 63, 55, 559; Arppe, *ibid.*, 1845, 64, 237; Schiff, *Annalen*, 1861, 119, 331; Bunsen, *ibid.*, 1866, 138, 277; Vogel, *Kastner's Archiv*, 1868, 23, 86.

The substance produced when one of the basic oxalates of bismuth, $\text{Bi}_2\text{O}(\text{C}_2\text{O}_4)_2$, is heated is a mixture, probably of bismuth monoxide and bismuth, but when the basic oxalate $\text{Bi}_2\text{O}_2 \cdot \text{C}_2\text{O}_4$ is heated in a current of carbon dioxide, bismuth monoxide alone is stated to be obtained : ¹



This method of Tanatar is now usually employed.

Bismuth trioxide is reduced by heating in a current of hydrogen ² at 267° C., or in carbon monoxide. In the former case it is possible that the monoxide is formed. In the latter case, the reduction being carried out at 300° C., it will be seen from the following data and the accompanying time-reduction curve (fig. 8) ³ that there is a break at

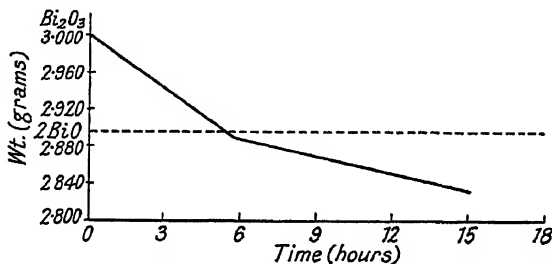


FIG. 8.—Reduction of Bismuth Trioxide by Carbon Monoxide at 300° C.

a point at which the composition of the reduction product corresponds approximately to that of bismuth monoxide.

Time (hours)	0	3	4½	6	9	12	15
Weight of Bi_2O_3 (grams)	3.000	2.934	2.920	2.890	2.868	2.850	2.831

The above methods and conclusions have, however, been criticised, and considerable doubt has been thrown on the existence of an oxide of bismuth lower than the trioxide.⁴

Bismuth monoxide is described as a greyish-black, finely crystalline powder, having a mean density ⁵ of 7.5 at 20° C., values lying between 7.17 and 8.55 having been reported. This value is lower than that of a corresponding mixture of bismuth trioxide and bismuth; but this does not prove the existence of a separate compound, as the low density may be due to the presence of hydroxide in the samples investigated.⁶

When dry, the oxide is quite stable in air, but in the presence of

¹ Tanatar, *Zeitsch. anorg. Chem.*, 1901, 27, 437; Denham, *J. Amer. Chem. Soc.*, 1921, 43, 2367.

² Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 21.

³ Brislee, *J. Chem. Soc.*, 1908, 93, 154.

⁴ Neusser, *Zeitsch. anorg. Chem.*, 1924, 135, 313; 138, 180; Vanino and Treubert, *Ber.*, 1898, 31, 1113, 2267; 1899, 32, 1072. See also Herz and Guttmann, *Zeitsch. anal. Chem.*, 1915, 54, 113, 413; *Zeitsch. anorg. Chem.*, 1907, 53, 63.

⁵ *International Critical Tables*, 1926, 1, 111. See also Treubert and Vanino, *Zeitsch. anal. Chem.*, 1914, 53, 564; 1915, 54, 255; Tanatar, *loc. cit.*

⁶ Neusser, *loc. cit.*

moist air it is slowly oxidised to a white hydrated trioxide, $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. It is also oxidised on heating in air, oxidation beginning at about 180°C . It is decomposed slowly by cold water, and more rapidly on boiling.

It is attacked by warm dilute acids with formation of salts of trivalent bismuth and precipitation of bismuth.¹ With hydrochloric acid this reaction may be represented by



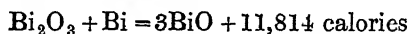
It is oxidised by nitric acid, but in the presence of excess of acid the reaction proceeds as with hydrochloric acid.

When heated in oxygen, oxidation begins at 140°C . and is complete at 240°C . The oxide is also oxidised slowly when heated in a current of carbon dioxide. It is easily reduced to metal by heating on a charcoal block, or in a current of hydrogen or carbon monoxide; reduction in hydrogen takes place at 300° to 310°C ., and in carbon monoxide begins at about 250°C .

The monoxide is readily oxidised on boiling with a solution of potassium hydroxide and bromine with the formation of the pentoxide, $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. It is converted to metal by reaction with aqueous potassium hydroxide alone. It will reduce Fehling's solution, and potassium permanganate.

It is weakly basic; the halide salts and the sulphide are the only salts derived from it that have been reported. They are unstable and difficult to obtain pure.

By comparing the heats of reaction of hydrochloric acid with bismuth monoxide and with a corresponding mixture of bismuth and bismuth trioxide, the calculated heat of formation of one mole of monoxide² is given as 3938 gram-calories, that is:



As has been stated previously, most of the facts enumerated here have been adversely criticised. Arguments have been brought forward in favour of the view that, on theoretical grounds, it is very improbable that bismuth monoxide can exist.³ Comparisons have been made between bismuth monoxide, prepared by various methods, and a corresponding mixture of bismuth and its trioxide; and the numerical values obtained for the heat evolved in the reaction with hydrochloric acid, the solubility in an aqueous solution of sodium hydroxide and the specific magnetic susceptibility⁴ have been found to be approximately identical in each case. In further support of this view, it is stated that metallic bismuth can be extracted from bismuth monoxide by shaking with mercury; and that the monoxide reacts with dry hydrogen sulphide as if it were a mixture of bismuth, bismuth trioxide and bismuth hydroxide.⁵ When prepared by the action of potassium hydroxide upon a solution of bismuth trioxide and stannous chloride in hydrochloric acid, it reacts with sulphur dioxide to form basic bismuth sulphate, $4\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$. Since this substance is also obtained

¹ Schneider, *loc. cit.*

² Tanatar, *loc. cit.*

³ Neusser, *loc. cit.*

⁴ See also Spencer, *J. Soc. Chem. Ind.*, 1930, 50, 37 T.

⁵ Neusser, *loc. cit.*

by the action of sulphur dioxide upon bismuth trioxide, it has been suggested that bismuth monoxide may be a compound $\text{Bi} \cdot \text{Bi}_2\text{O}_3$, but the possibility of its being merely a mixture of bismuth and trioxide is not eliminated.¹

Much of the confusion regarding the existence of bismuth monoxide undoubtedly arises from the difficulties encountered in the preparation and purification of specimens of the substance; the products obtained by the various methods described frequently vary in composition. In addition, these products are for the most part unstable, especially in the presence of moisture.²

Bismuth Trioxide or *Bismuth Sesquioxide*, Bi_2O_3 .—Bismuth trioxide is found naturally as bismuth ochre. It is the product obtained when bismuth burns in air ("*flores bismuti*"),³ or when steam is decomposed by metallic bismuth at white heat.⁴ It is usually obtained by the prolonged heating of molten bismuth in air, or by the action of heat upon the carbonate, sulphate or basic nitrate.⁵ Bismuth monoxide when heated in air yields the trioxide. The crystalline form is obtained by melting the powdered form with potassium hydroxide,⁶ by boiling the hydroxide with potassium or sodium hydroxide,⁷ by the action of potassium cyanide on a nitric acid solution of bismuth nitrate,⁸ or by adding sodium nitrate intermittently to a molten mixture of sodium hydroxide, bismuth and potassium chromate⁹ at 350° C. The oxide is also obtained when chlorine is passed into a fused mixture of bismuth and silver nitrate.¹⁰

The mineral, bismuth ochre, occurs in massive form with an uneven, earthy fracture; its colour is yellowish-grey or green; it is very soft and friable. The crystalline form of the oxide, prepared as described above, is obtained in the form of bright yellow, transparent rhombic prisms:¹¹

$$a : b : c = 0.817 : 1 : 1.065$$

More usually, bismuth trioxide is obtained as a lemon-yellow powder which becomes darker on heating. When pure it is insensitive to light.¹² The various values that have been given for the density and melting point of this oxide are probably due to the existence of polymorphism. Three varieties have been described. The first variety has a melting point at 820° C. and density 8.9. On cooling it passes to the second variety at 704° C. (density 8.2); supercooling frequently occurs at this transformation, followed by recalescence. This second variety varies from yellow to brown in colour. The third variety, melting at 860° C., and of density 8.5, is formed by heating the trioxide strongly in a porcelain crucible. Both the first and third varieties crystallise in the

¹ Hammick, *J. Chem. Soc.*, 1917, **III**, 383.

² See also Vanino and Zumbusch, *Arch. Pharm.*, 1910, 248, 665; Goldschmidt, *British Patent*, 1922, 189706.

³ v. Bonsdorff, *Pogg. Annalen*, 1837, **41**, 305.

⁴ Regnault, *Ann. Chim. Phys.*, 1836, [2], **62**, 263.

⁵ Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 360.

⁶ Nordenskiöld, *Pogg. Annalen*, 1861, **114**, 622.

⁷ Stromeyer, *Pogg. Annalen*, 1832, **26**, 533.

⁸ Muir and Hutchinson, *J. Chem. Soc.*, 1889, **55**, 143.

⁹ Tawara, *Japanese Patent*, 1931, 93504.

¹⁰ Darling, *U.S. Patent*, 1920, 1354806.

¹¹ Nordenskiöld, *Pogg. Annalen*, 1861, **114**, 622; Groth, *Chem. Kryst.*, 1906, **1**, 100, 109.

¹² Schiff, *Annalen*, 1861, **119**, 335; Schneider, *J. prakt. Chem.*, 1881, [2], **23**, 86.

rhombic system, but the first modification cannot exist at ordinary temperatures.¹

The variation of the specific heat of bismuth trioxide with the temperature is shown by the following data :

Temperature, ° C. .	50	100	200	300	400
Specific heat ² . .	0.0569	0.0593	0.0617	0.0631	0.0641

Temp., ° C. .	+16.3	-10.9	-59.7	-106.6	-160.0	-204.3	-212.4
Specific heat ³	0.0563	0.0561	0.0512	0.0447	0.0350	0.0241	0.0204

The variation of electrical resistivity with temperature ⁴ is :

Temperature, ° C. .	225	425	645
Resistivity (ohm-cm.) .	2.34×10^8	1.44×10^5	6.01×10^3

The thermoelectric power with reference to lead, between 500° and 800° C. and with the cold junction at 0° C., is given by

$$\text{Thermoelectric power} = (1.946 - 1.86t) \times 10^{-6} \text{ volt per degree C.}$$

where t is the temperature (° C.).⁵ The specific magnetic susceptibility ⁶ is -0.170×10^{-6} . The dielectric constant ⁷ is 18.2 and appears to be independent of the field strength.

Bismuth trioxide is volatile at high temperatures, the calculated boiling point being 1890° C. Volatilisation ⁸ begins at 950° C.

In the spectrum of bismuth trioxide ⁹ four band systems are found between 4300 and 6700 Å.

The heat of formation of the trioxide from its elements is 136,600 gram-calories per mole.¹⁰ The heats of formation of the hydrated forms of bismuth trioxide have also been calculated (see, however, p. 189).¹¹

The trioxide does not decompose when heated to 1750° C.¹² It is

¹ Guertler, *Zeitsch. anorg. Chem.*, 1903, 37, 222.

² Expressed as gram-calories per gram. Hauser and Steger, *Zeitsch. anorg. Chem.*, 1913, 80, 1. See also Regnault, *Ann. Chim. Phys.*, 1841, 1, 129.

³ Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2720. See also Kelley, *Bureau Mines Bulletin*, 1932, 350.

⁴ Horton, *Phil. Mag.*, 1906, 11, 505.

⁵ Bidwell, *Phys. Review*, 1914, 3, 204.

⁶ Endo, *Sci. Rep. Tohoku Imp. Univ.*, 1925, 14, 79.

⁷ Günther-Schulze and Keller, *Zeitsch. Physik*, 1932, 75, 78; Günther-Schulze and Betz, *ibid.*, 1931, 71, 106.

⁸ Feiser, *Metall und Erz*, 1930, 27, 585. See also Bailey, *J. Chem. Soc.*, 1887, 51, 680; Hempel, *Zeitsch. anal. Chem.*, 1881, 20, 449.

⁹ Ghosh, *Zeitsch. Physik*, 1933, 86, 241.

¹⁰ Mixer, *Amer. J. Sci.*, 1909, [4], 28, 103.

¹¹ Thomsen, "Thermochemistry" (London), 1908, p. 230.

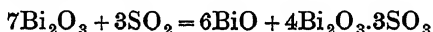
¹² Read, *J. Chem. Soc.*, 1894, 65, 313.

reduced, partially or completely, by a number of reducing agents, such as hydrogen,¹ carbon, carbon monoxide,² silicon,³ sodium, potassium, methane,⁴ ammonia, ammonium chloride, potassium cyanide,⁵ aluminium carbide,⁶ and an alkaline stannous solution. It is oxidised by ozone to bismuth pentoxide, and by ozone in the presence of alkalis to bismuthates;⁷ it is only slightly oxidised by alkaline permanganate solution.

When dry bismuth trioxide is heated in a current of dry chlorine, a white, crystalline, deliquescent sublimate of bismuth trichloride is formed. When heated with an excess of bromine for several hours, and after exposing the product to the air, an oxybromide, $\text{Bi}_{11}\text{O}_{13}\text{Br}_7$, is obtained as a non-deliquescent, cream-coloured powder.⁸

When heated with manganese dioxide, slight reaction takes place between 300° and 500° C. A violet-grey powder is formed, but the nature of the reaction has not been fully established.⁹

Bismuth trioxide reacts with sulphur to form bismuth trisulphide, and with hydrogen sulphide to form a sulphide¹⁰ to which has been ascribed the formula Bi_4S_3 . A rather complex reaction occurs with sulphur dioxide, among the products being a basic bismuth sulphate, and, possibly, bismuth monoxide.¹¹ The reaction may possibly be represented by the equation



It begins at a temperature below visible red heat. At first a dark grey or black powder is formed; this, on prolonged heating, is converted into the white, crystalline, basic sulphate, $4\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$. A little sulphur trioxide is also evolved. The dark grey powder contains a sulphate, but not a sulphide. It is not completely soluble in hydrochloric acid, and the black residue so produced is mainly bismuth. From this it is conjectured that the dark grey powder contains bismuth monoxide.

Bismuth trioxide does not appear to react with nitrogen, even when heated.¹² It is reduced to metal by heating with ammonia at 250° C. There is no indication of the formation of a bismuth nitride, but as some water is produced during the reaction it would appear that some of the ammonia is decomposed.¹³ The reduction is accelerated in the presence of silver and quartz sand. With phosphorus trichloride at 160° C. a complex reaction takes place, the products including bismuth oxychloride, bismuth phosphate, phosphorus oxychloride and perhaps bismuth dichloride.¹⁴ The trioxide is reduced by arsenic in the presence

¹ Schneider, *Pogg. Annalen*, 1851, 82, 312; Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 28.

² Muir, Hoffmeister and Robbs, *loc. cit.*; Brislee, *J. Chem. Soc.*, 1908, 93, 163.

³ Kahlenburg and Trautman, *Trans. Amer. Electrochem. Soc.*, 1921, 39, 412.

⁴ Müller, *Pogg. Annalen*, 1864, 122, 145.

⁵ Rose, *Pogg. Annalen*, 1853, 90, 199.

⁶ Pring, *J. Chem. Soc.*, 1905, 87, 1530.

⁷ Mailfert, *Compt. rend.*, 1882, 94, 863.

⁸ Muir, *J. Chem. Soc.*, 1877, 31, 26.

⁹ de Carli, *Atti R. Accad. Lincei*, 1926, [6], 4, 577.

¹⁰ Schumann, *Annalen*, 1877, 187, 313.

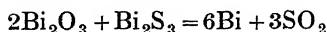
¹¹ Hammick, *J. Chem. Soc.*, 1917, 111, 385.

¹² Muir, *loc. cit.*, p. 647.

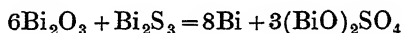
¹³ Muir, *loc. cit.*, p. 28. See also Gutbier and Brokenbach, *Zeitsch. Elektrochem.*, 1905, 11, 831.

¹⁴ Michaelis, *J. prakt. Chem.*, 1871, [2], 4, 454.

of molten sodium hydroxide.¹ It reacts readily with bismuth trisulphide according to the equation



The reaction begins at quite low temperatures in a current of carbon dioxide; it can also be conducted under molten sodium chloride. There remains, in addition, a residue which gives the reactions for a sulphate; probably partial reduction also takes place according to the equation²



Bismuth trioxide, when heated with silicon tetrachloride, yields bismuth trichloride and silica.³

It reacts with potassium thiocyanate⁴ with the formation of bismuth trisulphide and a complex compound, $\text{K}_2\text{Bi}_2\text{S}_4$.

Thermal examination of the system Bi_2O_3 -PbO reveals the possible existence of the compounds $4\text{Bi}_2\text{O}_3 \cdot \text{PbO}$ (decomposing at 690°C.), $3\text{Bi}_2\text{O}_3 \cdot 2\text{PbO}$ (M.pt. 686°C.) and $\text{Bi}_2\text{O}_3 \cdot 2\text{PbO}$ (M.pt. 625°C.) (see fig. 9).⁵

Bismuth trioxide does not attack platinum below 1200°C. in a neutral atmosphere. At 1300°C. it is slowly decomposed and the liberated bismuth gradually absorbed by the platinum with the formation of a brittle, fusible alloy. At 1400°C. this action becomes rapid, and a platinum vessel is completely destroyed when heated with bismuth trioxide at this temperature.⁶

Bismuth trioxide reacts mainly as a basic oxide, forming bismuth salts which, in most cases, are readily hydrolysed yielding, as the final product, basic salts. That, under certain conditions, it also exhibits very feeble acidic properties is shown by its slight solubility in aqueous solutions of alkali hydroxides, as indicated by the following data⁷ for the solubility in solutions of sodium hydroxide:—

Concentration of NaOH (moles per litre solution)	1.0	2.0	3.0
Solubility of Bi_2O_3 (grams per 100 c.c. solution)	0.0013 ± 0.0002	0.0026 ± 0.0002	0.0049 ± 0.0005

The solutions, in each case, give no indication of being colloidal. It will be seen that the solubility increases approximately in proportion to the concentration of the alkali. The feeble acidity of bismuth trioxide is further supported by the fact that in the solid state it will react with barium oxide when heated, but not with oxides less basic.⁸

Mixtures of bismuth trioxide and iron oxide (containing from 3 to 4 per cent. of bismuth trioxide) have been suggested as substitutes for

¹ Kirsebom, *French Patent*, 1930, 694283.

² Schoeller, *J. Soc. Chem. Ind.*, 1915, 34, 6.

³ Rauter, *Annalen*, 1892, 270, 251.

⁴ Milbauer, *Zeitsch. anorg. Chem.*, 1905, 42, 433.

⁵ Belladen, *Gazzetta*, 1922, 52, II, 160.

⁶ Kohlmeier and Westermann, *Siebert Festschr.*, 1931, 193; Feiser, *Metall und Erz*, 1930, 27, 585.

⁷ Knox, *J. Chem. Soc.*, 1909, 95, 1767.

⁸ de Carli, *Atti R. Accad. Lincei*, 1925, [6], 1, 533.

platinum gauze in the process for the catalytic oxidation of ammonia.¹ Similar mixtures of bismuth trioxide and cobalt oxide have also been employed. These oxide mixtures are used in the form of a loose, granular powder; they are active at about the same temperature as platinum gauze, but they act more slowly and their life is not so long.²

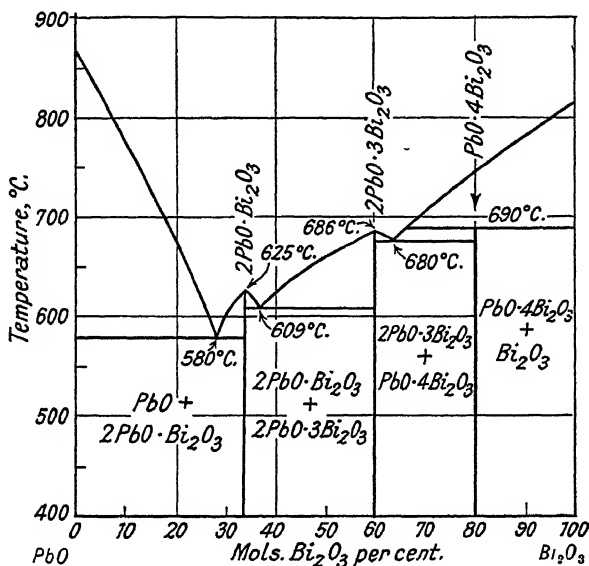


Fig. 9.—Freezing Point Diagram of the System Bi_2O_3 - PbO .

Bismuth Hydroxide or Hydrated Bismuth Trioxide.—Three hydrated forms of bismuth trioxide have been described. They are the *trihydrate*, or bismuth hydroxide, $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Bi}(\text{OH})_3$, the *dihydrate*, $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and the *monohydrate*, also known as bismuthyl hydroxide, $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{BiO}(\text{OH})$. There is no doubt that hydrated forms of the trioxide can be prepared by a variety of methods, but their existence as definite chemical compounds has been criticised. From a study of the dehydration of hydrated bismuth trioxide at a constant pressure of 10 mm. mercury, it was determined that water is removed in three stages. Assuming the original hydrated oxide to be the trihydrate, water is removed from this continuously as the temperature rises until the composition approximates to that of the dihydrate. At about 320°C . water is removed suddenly and the composition approaches that of the monohydrate. The remaining water is again removed continuously, a temperature higher than 420°C . being required for complete removal.³ An earlier investigation on the dehydration of the hydrated oxide by heating⁴ revealed a slight break in the dehydration

¹ Uchida, *J. Phys. Chem.*, 1926, 30, 1297; Hilditch, "Catalytic Processes in Applied Chemistry" (London, 1929), p. 127.

² For the use of bismuth trioxide as a filler in rubber compositions, see Williams, *U.S. Patent*, 1932, 1844306; for its use in the manufacture of glass, see Riegel and Sharp, *J. Amer. Ceramic Soc.*, 1934, 17, 88.

³ Hüttig, Tsuji and Steiner, *Zeitsch. anorg. Chem.*, 1931, 200, 74.

⁴ Carnelle and Walker, *J. Chem. Soc.*, 1888, 53, 86.

curve between 340° and 415° C., but no substance corresponding in composition to a definite hydrate was obtained. If the hydrated oxide is dried over sulphuric acid, dehydration proceeds continuously and there is no indication of a definite hydrate.¹ Further, recent attempts to prepare by various methods a substance that could be identified as the definite compound bismuth hydroxide, $\text{Bi}(\text{OH})_3$, have proved unsuccessful.² It is probable, therefore, that if definite hydrates of bismuth trioxide do exist, they are extremely unstable. The substance as usually prepared, and technically known as "bismuth hydroxide," is of indefinite composition. Among the methods adopted for its preparation may be mentioned precipitation from solutions of bismuth salts by ammonium hydroxide, followed by washing with a succession of volatile solvents and evaporation,³ and electrolysis of a dilute solution of sodium chlorate, containing carbon dioxide, using bismuth anodes and cathodes of carbon, zinc, iron or aluminium.⁴ A description follows of the three hydroxides that have been reported.

Bismuth Trihydrate, $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Bi}(\text{OH})_3$, is most conveniently prepared by adding a solution of a bismuth salt containing glycerol to one of sodium hydroxide, and neutralising the excess of alkali with nitric or acetic acid. The product is frequently contaminated with traces of the bismuth salt employed and with the carbonate (through absorption of carbon dioxide).⁵ The hydrate is not precipitated from solutions by alkalis in the presence of tartaric acid⁶ or citric acid.⁷ It is a white substance, and is converted to yellow bismuth trioxide on boiling with alkalis;⁸ at lower temperatures, in contact with alkalis, it is said to be converted to the monohydrate.⁹ At 20° C. it is practically insoluble in a normal solution of sodium hydroxide and more dilute solutions; the solubility is slightly higher in 4N NaOH, and increases appreciably with higher concentrations; it is greater at 100° C., but still low in dilute solutions.¹⁰ Thus bismuth hydroxide resembles the trioxide in possessing only very slight acidic properties. It is soluble in sodium hydroxide in glycerol,¹¹ and by heating this solution, and those in tartaric or citric acid, with grape sugar, the hydroxide is reduced to metal.

The so-called *dihydrate*, $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, is prepared as a pale yellowish-white, flocculent body by precipitation from a solution of so-called bismuthic acid in hydrochloric acid by potassium hydroxide after passing a current of sulphur dioxide through the liquid. When, however, sulphuric acid is used in place of hydrochloric acid, the precipitate is

¹ Moser, *Zeitsch. anorg. Chem.*, 1909, 61, 379. See, however, Thibault, *J. Pharm.*, 1900, [6], 12, 559.

² Hackspill and Kieffer, *Ann. Chim.*, 1930, [10], 14, 227.

³ I.G. Farbenind. A. G., *British Patent*, 1928, 332504.

⁴ Carreras, *British Patent*, 1927, 298587; *French Patent*, 1929, 640346; *German Patent*, 1927, 538286.

⁵ Moser, *loc. cit.*; Stromeyer, *Pogg. Annalen*, 1832, 26, 553; Muir and Carnegie, *J. Chem. Soc.*, 1887, 51, 79; Carnelley and Walker, *loc. cit.*

⁶ Schneider, *Pogg. Annalen*, 1854, 93, 312; Nylander, *Zeitsch. anal. Chem.*, 1884, 23, 440; Schmucker, *Zeitsch. anorg. Chem.*, 1894, 5, 206.

⁷ Smith and Frankel, *Amer. Chem. J.*, 1890, 12, 428; Lottermoser, *J. prakt. Chem.*, 1899, [2], 59, 489; Rosenheim and Vogelsang, *Zeitsch. anorg. Chem.*, 1906, 48, 208.

⁸ Stromeyer, *loc. cit.*

⁹ Moser, *loc. cit.* See, however, Corfield and Woodward, *Chemist and Druggist*, 1924, 101, 134.

¹⁰ Moser, *loc. cit.* See also Knoevenagel and Ebler, *Ber.*, 1902, 35, 3055.

¹¹ Löwe, *Zeitsch. anal. Chem.*, 1871, 10, 452.

more probably the monohydrate.¹ Two dimorphous forms of the dihydrate have been described.²

The *monohydrate*, or *bismuthyl hydroxide*, or "*bismuthi hydroxidum*," $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{BiO}(\text{OH})$, is prepared by pouring a solution of bismuth nitrate in dilute nitric acid rapidly into ammonium hydroxide and drying the precipitate at a temperature not exceeding 70°C .³ This method has, however, been criticised on the grounds that the hydroxide always contains either an oxy-salt or the trioxide; it is also stated that the only true hydroxide is the trihydrate, $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. On heating to 110°C . the trihydrate loses water, the residue containing 94 per cent. of the trioxide.⁴ The monohydrate is soluble in ordinary distilled water to the extent of 1.44 milligrams per litre at 20°C .⁵ It will precipitate the hydroxides of aluminium, chromium and ferric iron from neutral solutions of their salts, but is apparently without effect upon solutions of copper, zinc, ferrous iron, nickel, cobalt, manganese and lead;⁶ but according to other investigators the monohydrate precipitates most metals as oxides or basic salts. It can be oxidised in alkaline solution by many oxidising agents and is reduced by stannous solution to bismuth monoxide.

Colloidal hydrated bismuth oxides, known as "*bismon*," have been obtained,⁷ while hydrosols have also been prepared.⁸

Higher Oxides of Bismuth.

Various higher oxides of bismuth have been described from time to time, although in many cases it is uncertain that the substances obtained were pure. Three of these oxides will be discussed here, namely, *bismuth tetroxide*, Bi_2O_4 , *bismuth pentoxide*, Bi_2O_5 , and *bismuth hexoxide*, Bi_2O_6 .

As early as 1818 an oxide of bismuth containing more oxygen than the trioxide was prepared,⁹ but this, and many of the preparations subsequently described by other investigators, were probably mixtures of the tetroxide and the pentoxide, and may even in some cases have contained an alkali bismuthate. In most cases the higher oxide was prepared by the action of an oxidising agent upon a suspension of the trioxide in an alkaline solution. Oxidising agents that have been employed include ozone,¹⁰ hydrogen peroxide,¹¹ potassium persulphate,¹²

¹ Muir, *J. Chem. Soc.*, 1877, 31, 647.

² Moser, *loc. cit.*

³ "*British Pharmaceutical Codex*," 1923, p. 207; Arppe, *Pogg. Annalen*, 1864, 64, 237; Thibault, *J. Pharm. Chim.*, 1900, [6], 12, 559; Muir, *J. Chem. Soc.*, 1877, 31, 648.

⁴ Corfield and Woodward, *Pharm. J.*, 1924, 113, 83, 128; *Chemist and Druggist*, 1924, 101, 134.

⁵ Almkvist, *Zeitsch. anorg. Chem.*, 1918, 103, 240.

⁶ Lebaigue, *J. Pharm.*, 1861, [3], 39, 51.

⁷ Paal and di Pol, *Ber.*, 1926, 59 B, 874.

⁸ Biltz, *Ber.*, 1902, 35, 4434; Kuhn and Pirsch, *Kolloid Zeit.*, 1925, 36 (*Zsigmondy-Festschrift*), 310; Haissinsky, *Compt. rend.*, 1934, 198, 580.

⁹ Bucholz and Brandes, *Schweigger's J.*, 1818, 22, 23.

¹⁰ Schönbein, *J. prakt. Chem.*, 1864, 93, 59; Mailfert, *Compt. rend.*, 1882, 94, 863.

¹¹ Hasebroek, *Ber.*, 1887, 20, 213; Jannasch and collaborators, *Ber.*, 1893, 26, 1499, 2908; 1894, 27, 2227; 1895, 28, 994, 1408; *Zeitsch. anorg. Chem.*, 1895, 8, 302; Morath and Lorch, *Inaug. Dissertation, München*, 1893; Rupp and Schaumann, *Zeitsch. anal. Chem.*, 1903, 42, 732; Hauser and Vanino, *Zeitsch. anorg. Chem.*, 1904, 39, 381; Moser, *Zeitsch. anorg. Chem.*, 1906, 50, 33.

¹² Deichler, *Zeitsch. anorg. Chem.*, 1899, 20, 81; Rupp, *Zeitsch. anal. Chem.*, 1903, 42, 732.

alkali hypochlorite,¹ chlorine, bromine,² and potassium ferricyanide.³ Molten bismuth trioxide has also been oxidised by air, potassium chlorate and potassium nitrate.⁴ In addition, higher oxides have been obtained by electrolytic methods.⁵

Many of the methods just mentioned, involving the oxidation of bismuth trioxide in the presence of alkalis, have been repeated,⁶ but in no case was a compound of uniform composition obtained; and the compound previously considered to be bismuthic acid, HBiO_3 ,⁷ always contained less oxygen than corresponds with this formula and was not uniform in composition, and further the product shows no sign of salt formation with a concentrated solution of potassium hydroxide. Probably the product obtained is a mixture of higher oxides which possess no acidic properties. Attempts to obtain a uniform product by electrolytic methods have also proved unsuccessful.⁸

Bismuth Tetroxide, Bi_2O_4 , hydrated with one or two molecules of water, is formed when sodium bismuthate is decomposed with nitric acid; the anhydrous substance has not been obtained by this method, as oxygen is lost when water is removed.⁹

Four different modifications have been obtained by the action of various oxidising agents upon a suspension of bismuth trioxide in boiling solutions of dilute alkali hydroxides.¹⁰ Two of these modifications are anhydrous, the others being modifications of the monohydrate, $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$. A dihydrate, $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is obtained by the action of chlorine upon a suspension of trioxide in a boiling, concentrated solution of alkali hydroxide; it is always contaminated with a hydrated pentoxide, from which it can be separated by treatment with boiling, concentrated nitric acid.

Anhydrous bismuth tetroxide is brown or purplish-black. Its density (at 20°C .) is 5.60 to 5.75, that of the dihydrate being 5.80. The anhydrous substance is stable at 100°C ., but loses oxygen at 160°C . The monohydrates begin to lose water at 100°C ., and are decomposed at 160°C ., whilst the dihydrate is decomposed at 100°C ., losing both oxygen and water. The tetroxide is not attacked by dilute nitric or

¹ Brandes, *Schweigger's J.*, 1833, 69, 158; Stromeyer, *Pogg. Annalen*, 1832, 26, 549; Jacquelin, *Ann. Chim. Phys.*, 1837, [2], 66, 113; *J. prakt. Chem.*, 1838, 14, 1; Arppe, *Pogg. Annalen*, 1845, 64, 238; Schrader, *Annalen*, 1862, 121, 204; Schiff, *Annalen*, 1861, 119, 342; Rupp, *Zeitsch. anal. Chem.*, 1903, 42, 732; Foster, *Ber.*, 1879, 12, 846.

² Jacquelin, *loc. cit.*; Arppe, *loc. cit.*; Heintz, *Pogg. Annalen*, 1844, 63, 55, 559; Schiff, *loc. cit.*; Schrader, *loc. cit.*; Hoffmann, *Annalen*, 1884, 223, 110; Muir, *J. Chem. Soc.*, 1876, 29, 149; Hilger and van Scherpenberg, *Mitteilungen aus der Erlanger Pharm. Inst.*, 1889, II, 4, 7; Morath and Lorch, *loc. cit.*; Deichler, *Zeitsch. anorg. Chem.*, 1899, 20, 81, 103; André, *Compt. rend.*, 1891, 113, 860; 1892, 114, 359.

³ Hauser and Vanino, *loc. cit.*

⁴ Bucholz and Brandes, *loc. cit.*; Jacquelin, *loc. cit.*; Frémy, *Compt. rend.*, 1842, 15, 1108; Schneider, *Monatsh.*, 1888, 9, 252; Bottger, *J. prakt. Chem.*, 1858, 73, 494.

⁵ Luckow, *Dingl. poly. J.*, 1865, 177, 231; Wernicke, *Pogg. Annalen*, 1870, 141, 117; Schucht, *Berg- und Hütten-männische Zeitung*, Leipzig, 1880, 121; Deichler, *loc. cit.*; Holland, *Compt. rend.*, 1903, 136, 229; Bose, *Zeitsch. anorg. Chem.*, 1905, 44, 237; Grube and Schweigardt, *Zeitsch. Elektrochem.*, 1923, 29, 257.

⁶ Gutbier and Bünz, *Zeitsch. anorg. Chem.*, 1906, 48, 162; 1906, 49, 432; 1906, 50, 210; 1907, 52, 124; *Sitzungsberichte physikal.-med. Soz. Erlangen*, 1909, 40, 90; *Chem. Zentr.*, 1909, i, 732.

⁷ Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 22; Deichler, *loc. cit.*

⁸ Gutbier and Bunz, *Zeitsch. anorg. Chem.*, 1906, 48, 294. See also Muir, *J. Chem. Soc.*, 1876, 29, 151.

⁹ Corfield and Woodward, *Pharm. J.*, 1923, [4], 56, 80; *Chemist and Druggist*, 1923, 99, 134; "Yearbook of Pharmacy," 1923, 570.

¹⁰ Worsley and Robertson, *J. Chem. Soc.*, 1920, 117, 63.

sulphuric acid. The crude substance as usually prepared is partially dissolved by more concentrated nitric acid (density 1.2) at 70° to 90° C., with evolution of oxygen, the insoluble residue having a composition corresponding to that of bismuth tetroxide. From this it is deduced that the usual preparations are mixtures, probably of tetroxide and pentoxide. The tetroxide reacts with concentrated oxygen acids to form tervalent bismuth salts with evolution of oxygen. It is very sparingly soluble in alkali hydroxide.

Bismuth tetroxide can be reduced by hydrogen and by carbon monoxide. Hydrogen peroxide is decomposed by it.¹ It is a powerful oxidising agent; hydrochloric acid is oxidised to chlorine even at -15° C., and manganous salts are oxidised to permanganate immediately in the cold in the presence of nitric acid.

With hydrochloric acid there is no indication of the formation of a chloride of quadrivalent bismuth.²

Bismuth Pentoxide, Bi_2O_5 , or a hydrated form of this compound, is probably formed, mixed with tetroxide, by most of the methods already mentioned. Bismuthic acid, HBiO_3 , is said to be formed when a solution of bismuth oxytrifluoride, BiOF_3 , is decomposed by water and nitric acid, and evidence of the formation of sodium bismuthate was also obtained when the same compound was treated with sodium hydroxide.³ A hydrated oxide, $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$, is obtained either by the action of chlorine on bismuth trioxide suspended in a boiling concentrated solution of alkali hydroxide or, in small quantities, by the action of ammonium persulphate on the trioxide suspended in dilute alkali at 40° to 60° C. for five or six hours. In both cases the pentoxide is mixed with hydrated tetroxide. Two varieties of the monohydrate of the pentoxide have been described, a red or brown variety soluble only with difficulty in concentrated nitric acid, and a brown variety, obtained from commercial sodium bismuthate after repeatedly grinding with glacial acetic acid, which is readily soluble in nitric acid (density 1.2). The hydrate rapidly decomposes at 100° C., leaving a residue of trioxide and tetroxide. It is possible that the anhydrous form is incapable of existence.⁴

Bismuth pentoxide is described as a dark red powder of density (at 20° C.) 5.10; on heating it loses oxygen, yielding first the tetroxide and finally the trioxide. It is reduced by hydrogen and by carbon monoxide; it is an oxidising agent, but has only feeble acidic properties.

Bismuthates of sodium and potassium have been described. Sodium bismuthate can be prepared by adding basic bismuth nitrate gradually to caustic soda heated to redness; sodium peroxide is then added and the fused mass is allowed to cool.⁵ Many earlier investigators mentioned and described alkali bismuthates, obtained by the methods outlined for the preparation of higher oxides, but it is doubtful whether the substances obtained were pure, or were even true compounds.⁶ Sodium bismuthate as made commercially is a very unstable substance, being

¹ Schönbein, *J. prakt. Chem.*, 1864, 93, 59.

² Hauser and Vanino, *Zeitsch. anorg. Chem.*, 1904, 39, 381.

³ Ruff, Knoch and Zedner, *Zeitsch. anorg. Chem.*, 1908, 57, 220. See, however, Gutbier and Micheler, *Zeitsch. anorg. Chem.*, 1908, 59, 143.

⁴ Worsley and Robertson, *J. Chem. Soc.*, 1920, 117, 63.

⁵ Reddrop and Ramage, *J. Chem. Soc.*, 1895, 67, 271; Corfield and Woodward, *Pharm. J.*, 1923, [4], 56, 80; "Yearbook of Pharmacy," 1923, 570.

⁶ Jacquelin, *J. prakt. Chem.*, 1838, 14, 1; Muir, *J. Chem. Soc.*, 1878, 33, 197.

decomposed by hot water and by dilute acids. It is used as an oxidising agent in the analytical determination of manganese in iron and steel alloys, the manganese being oxidised in the cold to permanganate in the presence of nitric acid.

Bismuth Hexoxide, Bi_2O_6 , has been obtained in small quantities by the action of ammonium persulphate or potassium ferricyanide upon a suspension of trioxide in a boiling concentrated solution of alkali hydroxide. Bismuth tetroxide is formed at the same time, and separation may be effected by treatment with warm nitric acid (density 1.2). It may also be obtained by the oxidation of bismuth trioxide. It is a pale brown, anhydrous substance, which loses oxygen slowly at the ordinary temperature.¹

Evidence suggesting the existence of another oxide, Bi_4O_7 , has been obtained from a study of the electrode $\text{Bi}/\text{Bi}_2\text{O}_3$ in solutions of sodium hydroxide in the presence of oxidising agents.² This oxide does not appear to have been isolated, however.

BISMUTH AND SULPHUR.

Bismuth and sulphur combine when heated together. Two sulphides have been described; they are, bismuth monosulphide, BiS or Bi_2S_2 , and bismuth trisulphide, Bi_2S_3 . No evidence has yet been obtained in favour of a sulphide higher than the trisulphide.³ Bismuth trisulphide is the more stable compound of the two; indeed, the view has been put forward that the monosulphide is really a mixture of the trisulphide and metal.⁴ An examination of the freezing point curve of mixtures of bismuth and sulphur (fig. 10) fails to reveal any indication of the existence of bismuth monosulphide.⁵ A brief description of the results of investigations on this substance, however, follows.

Bismuth Monosulphide, BiS , is stated to be formed when hydrogen sulphide acts upon bismuth monoxide, either directly or in a solution containing stannous compounds and tartaric acid;⁶ also by heating a mixture of bismuth hydroxide with an aqueous solution of potassium cyanide and thiocyanate.⁷ Crystals have been obtained by melting together bismuth and sulphur and cooling the melt quickly. These crystals are stated by some to be bismuth monosulphide and by others to be a mixture of trisulphide and metal.⁸

When prepared in the dry way, the product is a slate-grey powder with a density of 7.6 to 7.8 at 20° C.; prepared in the wet way it is a black, dull powder, which can be obtained in the anhydrous form by drying over sulphuric acid. When dried over a water-bath some water is still retained.⁹

¹ Worsley and Robertson, *loc. cit.*

² Baur and Lattmann, *Zeitsch. Elektrochem.*, 1934, 40, 582.

³ Muir, *J. Chem. Soc.*, 1878, 33, 199.

⁴ Moser and Neusser, *Chem. Zeit.*, 1923, 47, 541, 581.

⁵ *International Critical Tables*, 1928, 4, 25; Pélabon, *Ann. Chim. Phys.*, 1909, 17, 526; *Compt. rend.*, 1903, 137, 648; Aten, *Zeitsch. anorg. Chem.*, 1905, 47, 386; Herz and Guttmann, *ibid.*, 1907, 53, 71.

⁶ Schneider, *J. prakt. Chem.*, 1899, [2], 60, 524; *Pogg. Annalen*, 1856, 97, 480; Herz and Guttmann, *Zeitsch. anorg. Chem.*, 1907, 53, 71.

⁷ Hoffmann, *Annalen*, 1884, 223, 134.

⁸ Werther, *J. prakt. Chem.*, 1842, 27, 65; Heintz, *Pogg. Annalen*, 1844, 63, 57; Schneider, *Pogg. Annalen*, 1854, 91, 404; Rose, *Pogg. Annalen*, 1854, 91, 401; Vanino and Treubert, *Ber.*, 1899, 32, 1078; Schneider, *J. prakt. Chem.*, 1899, [2], 60, 524; Herz and Guttmann, *loc. cit.*

⁹ Schneider, *Pogg. Annalen*, 1856, 97, 480.

The monosulphide is moderately stable in air, but it yields sulphur dioxide when heated in air. It is attacked by hydrochloric acid, bismuth trichloride being formed in solution and spongy metallic bismuth precipitated. It is decomposed into metal and trisulphide when heated to red heat in dry carbon dioxide.

Bismuth Trisulphide, or *Bismuth Sesquisulphide*, Bi_2S_3 , is found free in nature as *bismuthinite*, or *bismuth glance*. It may be made

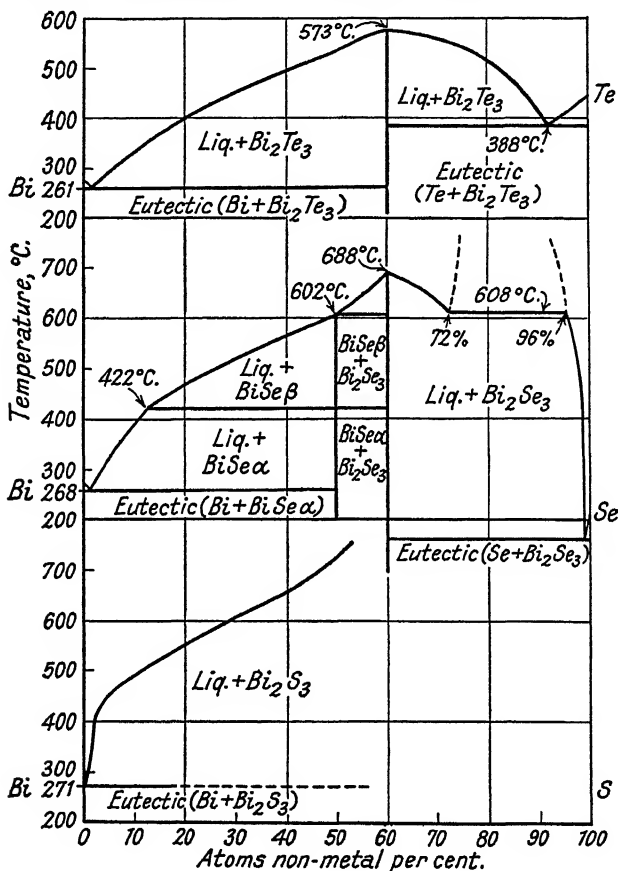


FIG. 10.—Freezing Point Diagrams of the Systems Bi-S, Bi-Se, Bi-Te.

artificially in a variety of ways, such as by melting together bismuth and sulphur,¹ by subjecting a mixture of bismuth and sulphur in powder form to high pressure,² by precipitation from a solution of a bismuth salt by hydrogen sulphide or alkali sulphide, by the action of sodium thiosulphate on a neutral solution of a bismuth salt,³ or by heating bismuth trioxide with potassium thiocyanate.⁴ In addition, it may be

¹ Lagerhjelm, *Schweigger's J.*, 1816, 17, 417; Rössler, *Zeitsch. anorg. Chem.*, 1895, 9, 44; Aten, *Zeitsch. anorg. Chem.*, 1905, 47, 386.

² Spring, *Ber.*, 1883, 16, 1001.

³ Faktor, *Pharm. Post*, 1900, 33, 301.

⁴ Milbauer, *Zeitsch. anorg. Chem.*, 1905, 42, 441.

prepared from bismuth halides by the methods described on pp. 173, 181. It may be obtained in the crystalline form by the interaction of the vapour of bismuth trichloride with hydrogen sulphide.¹

Bismuth trisulphide crystallises in the rhombic system, although other crystal forms have been described.² The crystal elements of the mineral bismuthinite are:³

$$a : b : c = 0.9862 : 1 : 1.0493$$

By X-ray examination it is deduced that the unit cell contains four molecules. The parameters⁴ have been determined to be :

$$a = 11.13 \text{ \AA.}, \quad b = 11.27 \text{ \AA.}, \quad c = 3.97 \text{ \AA.}$$

giving as axial ratios :

$$a : b : c = 0.9876 : 1 : 0.3523$$

As usually prepared the sulphide is a grey or black powder, which can be converted into a microcrystalline mass by heat, by pressure, or by heating in a solution of alkali sulphide.⁵ It has a density of 7.00 to 7.81; that of bismuthinite is 7.4 at 20° C.

The melting point⁶ is 718° C. By heating strongly in an atmosphere of carbon dioxide it can be volatilised in small quantities without decomposition.⁷

The compressibility of bismuthinite⁸ has been measured. The heat capacity⁹ is 0.06 gram-calorie per gram. When examined with light from an electric arc, bismuth trisulphide shows very great photoconductivity (*i.e.* an alteration in electrical conductivity on exposure to light).¹⁰

Bismuth trisulphide is only very slightly soluble in water, the solubility,¹¹ measured by a conductivity method, being 0.85×10^{-6} mole per litre. It is slightly soluble in dilute hydrochloric acid, the solubility increasing rapidly with rise of temperature. With dilute acid hydrogen sulphide is evolved at about 70° C., but the temperature of evolution is dependent on the concentration of the acid. The trisulphide is readily soluble in concentrated hydrochloric acid.¹² It is readily attacked by dilute nitric acid, sulphur being precipitated. It is decomposed by heating with sulphuric acid, sulphur dioxide being evolved. It is slightly soluble in sulphurous acid,¹³ but insoluble in an aqueous solution of sodium sulphite. It is insoluble in aqueous solutions of alkali hydroxides, but is soluble in solutions of alkali sulphides, the solubility increasing rapidly with increase in concentration of the alkali sulphide. From the accompanying table it will be seen that this solubility is

¹ Durocher, *Compt. rend.*, 1851, 32, 823.

² Phillips, *Pogg. Annalen*, 1827, 11, 476; Rossler, *Zeitsch. anorg. Chem.*, 1895, 9, 31.

³ Peacock, *Zeitsch. Krist.*, 1933, 86, 203.

⁴ Hofmann, *Zeitsch. Krist.*, 1933, 86, 225.

⁵ Sprng, *Zeitsch. physikal. Chem.*, 1895, 18, 556; Senarmont, *Ann. Chim. Phys.*, 1851, [3], 32, 129; Ditte, *Compt. rend.*, 1895, 120, 186.

⁶ Borgstrom, *Nord Kemistmetod*, 1928, 169.

⁷ Schneider, *Pogg. Annalen*, 1854, 91, 420.

⁸ Madelung and Fuchs, *Annalen der Physik*, 1921, 65, 289.

⁹ Regnault, *Ann. Chim. Phys.*, 1841, 1, 129.

¹⁰ Case, *Phys. Review*, 1917, 9, 305.

¹¹ Weigel, *Zeitsch. physikal. Chem.*, 1907, 53, 293.

¹² Ramachandran, *Chem. News*, 1925, 131, 135, 294, 386.

¹³ Guerout, *Compt. rend.*, 1872, 75, 1276.

increased by the presence of alkali hydroxides.¹ Bismuth trisulphide is, however, insoluble in alkali hydrosulphides; this is demonstrated by the fact that when a solution of the trisulphide in a solution of alkali sulphide is saturated with hydrogen sulphide, the trisulphide is completely reprecipitated. The trisulphide is also insoluble in solutions of ammonium sulphide. In addition, the solubility in solutions of sodium disulphide is very much less than in corresponding solutions of sodium monosulphide. It is probable, therefore, that the solubility of bismuth trisulphide in solutions of alkali sulphides is due to the formation of complex anions with the sulphide ion, $S^{=}$, and that complex anions with either the hydrosulphide ion, SH^{-} , or the hydroxyl ion, OH^{-} , are not formed.

Bismuth does not appear to form a hydrosulphide.²

SOLUBILITY OF BISMUTH TRISULPHIDE IN AQUEOUS SOLUTIONS OF ALKALI SULPHIDES AT 25° C.

Concentration of Aqueous Solutions used as Solvents (Moles per litre).				Solubility of Bismuth Trisulphide (Grams per 100 c.c. Solution).
Sodium Monosulphide.	Sodium Hydroxide.	Potassium Monosulphide.	Potassium Hydroxide.	
0.5	0.0040
1.0	0.0238
1.5	0.1023
0.5	1.0	0.0185
1.0	1.0	0.0838
..	..	0.5	..	0.0042
..	..	1.0	..	0.0337
..	..	1.5	..	0.0639
..	..	0.5	1.0	0.0240
..	..	1.0	1.0	0.1230
..	..	1.25	1.25	0.2354

Bismuth trisulphide is stable in air at temperatures up to 100° C.;³ above that temperature it begins to lose weight; sulphur is removed on melting, and on cooling crystals of bismuth can be detected in the mass;⁴ it is completely desulphurised by heating in the electric furnace.⁵ It is very slowly reduced by heating in a current of hydrogen,⁶ and the conditions of equilibrium between bismuth trisulphide and hydrogen⁷ have

¹ Knox, *J. Chem. Soc.*, 1909, 95, 1760. See also Abegg, *Zeitsch. anorg. Chem.*, 1904, 39, 330; Abegg and Bodlander, *ibid.*, 1899, 20, 453; Stillman, *J. Amer. Chem. Soc.*, 1896, 18, 683; Stone, *ibid.*, 1896, 18, 1091.

² Linder and Picton, *J. Chem. Soc.*, 1892, 61, 132.

³ Rose, *Pogg. Annalen*, 1860, 110, 136.

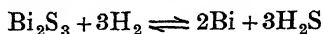
⁴ Marx, *Schweigger's J.*, 1830, 58, 472; 1830, 59, 114; Schneider, *Pogg. Annalen*, 1854, 91, 420. See also Schoeller, *J. Soc. Chem. Ind.*, 1915, 34, 6, 9.

⁵ Mourlot, *Compt. rend.*, 1897, 124, 768.

⁶ Rose, *Pogg. Annalen*, 1860, 110, 136.

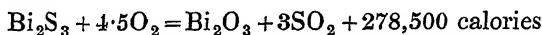
⁷ Britske and Kapustinski, *Tsvet. Met.*, 1931, 1147; *Zeitsch. anorg. Chem.*, 1930, 194, 323.

been studied between 400° and 1000° C. The effect of the presence of alkaline earth sulphides upon the equilibrium



has also been studied.¹ Calcium sulphide appears to be without effect, but the presence of sulphides of strontium and barium retards the decomposition of bismuth trisulphide.

The trisulphide is oxidised when heated in air or oxygen; it is difficult, however, to eliminate all the sulphur unless the heating is carried out *in vacuo*.² The presence of excess of bismuth trioxide also facilitates the removal of sulphur. The calculated heat of oxidation of bismuth trisulphide³ is:



The trisulphide, when red hot, will decompose steam; the products of the reaction are bismuth, bismuth trioxide and hydrogen sulphide.⁴

No reaction occurs on heating with ammonium chloride.⁵

The trisulphide is reduced by phosphine to metallic bismuth; phosphorus and hydrogen sulphide are also formed by this reaction.⁶

Reduction to the metal occurs by heating on a charcoal block, the reduction being accelerated by the presence of sodium carbonate. On passing a mixture of air and carbon tetrachloride over heated bismuth trisulphide, bismuth trichloride volatilises.⁷

When heated with sulphur dioxide, bismuth sulphate and metallic bismuth are formed.⁸

The sulphide does not react with a solution of potassium cyanide,⁹ but it is completely reduced to metal when heated in the dry state with that salt.¹⁰

Freshly precipitated bismuth trisulphide reacts when boiled with an aqueous solution of cuprous chloride and sodium chloride to form bismuth trichloride and cuprous sulphide; the trichloride is subsequently hydrolysed. When boiled with a dilute aqueous solution of cupric chloride, cupric sulphide and bismuth trichloride are formed in a similar manner. In each case the bismuth trichloride may be partially hydrolysed.¹¹ An investigation into the action of solutions of various metallic salts upon various metallic sulphides—including bismuth trisulphide—indicated that the affinity of bismuth for sulphur is greater than that of any other element in the fifth group of the Periodic Classification, and is also greater than that of lead.¹²

By treatment of bismuth trisulphide with a cold, saturated, ammoniacal solution of mercuric cyanide, bismuth cyanide and mercuric sulphide are formed; the latter is volatilised on heating, and the

¹ Schenck and Pardun, *Zeitsch. anorg. Chem.*, 1933, 211, 209.

² Schenck and Speckmann, *Zeitsch. anorg. Chem.*, 1932, 206, 378.

³ Britske and Kapustinski, *loc. cit.*

⁴ Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 382.

⁵ de Clermont, *Compt. rend.*, 1879, 88, 973.

⁶ Rose, *Pogg. Annalen*, 1830, 20, 336.

⁷ Braddock-Rogers, *Chem. News*, 1929, 138, 147.

⁸ Milbauer and Tucek, *Chem. Zeit.*, 1926, 50, 323.

⁹ Hoffmann, *Annalen*, 1884, 223, 134.

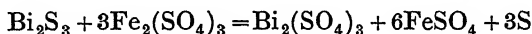
¹⁰ Rose, *Pogg. Annalen*, 1854, 91, 104; 1860, 110, 136.

¹¹ Raschig, *Ber.*, 1884, 17, 697; *Annalen*, 1885, 228, 18.

¹² Schürmann, *Annalen*, 1888, 249, 326.

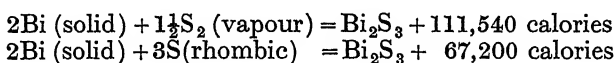
former decomposed, the resultant bismuth metal being oxidised to trioxide by heating in air.¹

The trisulphide reacts with ferric chloride in a sealed tube; bismuth trichloride and ferrous chloride are formed and some sulphur is set free.² With ferric sulphate a reaction takes place according to the equation



The ferrous sulphate thus formed can be estimated by titration with potassium permanganate and the method used for the volumetric estimation of the trisulphide.³

The following heats of formation from solid bismuth and sulphur vapour, and from solid bismuth and solid (rhombic) sulphur, have been calculated: ⁴



Colloidal bismuth trisulphide may be obtained by passing hydrogen sulphide through a very weak solution of bismuth nitrate, acidified with acetic acid, and dialysing.⁵

Thiobismuthites.—Several compounds of bismuth trisulphide with other metallic sulphides have been described, and certain minerals which contain bismuth sulphide in association with sulphides of copper, silver or lead are stated to be complex compounds of this type; some of these have been made artificially.⁶ By melting together metallic bismuth, sulphur and alkali carbonate, Schneider claimed to have produced complex sulphides with alkalis,⁷ but attempts to repeat this preparation proved unsuccessful.⁸ On the other hand, reactions have been described between bismuth trisulphide and sulphides of the alkaline earth metals⁹ which have resulted in the formation of the thiobismuthites SrBi_2S_4 and BaBi_2S_4 . The corresponding compound of calcium has not been obtained. The calculated heat of formation of the strontium compound is 4173 gram-calories, that of the barium compound being 13,380 gram-calories per mole.

Thermal examinations of binary systems of bismuth trisulphide with other metallic compounds have been made, including the system with antimony trisulphide,¹⁰ bismuth telluride¹¹ and silver selenide.¹² The results are summarised¹³ in fig. 11.

¹ Schmidt, *Ber.*, 1894, 27, 225.

² Cammerer, *Berg. Hütten. Zeitung*, 1891, 50, 295; *Chem. Zentr.*, 1891, ii, 525.

³ Hanus, *Zeitsch. anorg. Chem.*, 1898, 17, 111.

⁴ Britske and Kapustinski, *Zeitsch. anorg. Chem.*, 1930, 194, 323; *Tsvet. Met.*, 1931, 1147.

⁵ Winssinger, *Bull. Acad. Belg.*, 1888, [3], 15, 403.

⁶ Schneider, *J. prakt. Chem.*, 1889, [2], 40, 564; Rössler, *Zeitsch. anorg. Chem.*, 1895, 9, 47.

⁷ Schneider, *Pogg. Annalen*, 1869, 136, 464; 1869, 138, 309.

⁸ Muir, *J. Chem. Soc.*, 1878, 33, 199. See also Ditté, *Compt. rend.*, 1895, 120, 186; Milbauer, *Zeitsch. anorg. Chem.*, 1905, 42, 441.

⁹ Schenck and Pardun, *Zeitsch. anorg. Chem.*, 1933, 211, 209. See also Schenck, *ibid.*, 1933, 211, 203.

¹⁰ Takahashi, *Mem. Coll. Sci. Kyōto*, 1919, 4, 47.

¹¹ Amadori, *Atti R. Accad. Lincei*, 1915, 24, II, 200.

¹² Pélabon, *Compt. rend.*, 1908, 146, 975.

¹³ See also *International Critical Tables*, 1928, 4, 47, 48.

The ternary system bismuth-sulphur-tellurium has also been investigated,¹ the results pointing to the existence of one ternary compound only, $\text{Bi}_4\text{S}_3\text{Te}_3$ or $\text{Bi}_2\text{S}_3 \cdot \text{Bi}_2\text{Te}_3$. Several minerals are known

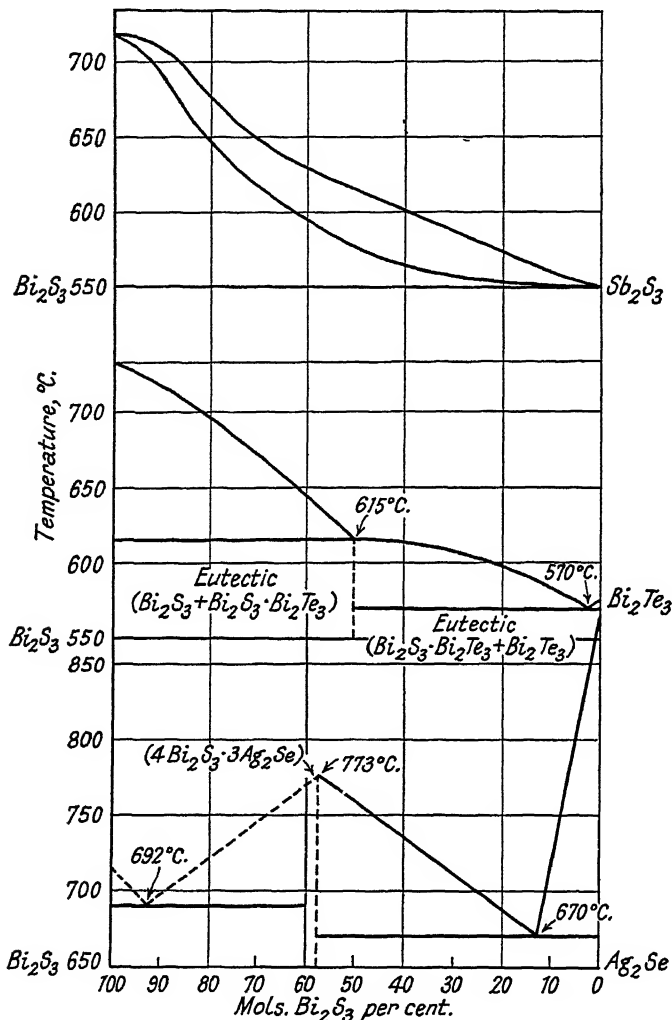


FIG. 11.—Freezing Point Curves of the Systems Bi_2S_3 - Sb_2S_3 , Bi_2S_3 - Bi_2Te_3 , Bi_2S_3 - Ag_2Se .

containing bismuth, sulphur and tellurium, but their constitution is unknown. *Oruetite*, to which the formula $\text{Bi}_3\text{S}_4\text{Te}$ has been ascribed, is revealed as a mixture (or solid solution) when examined by X-rays.

¹ Garrido, *Anal. Fis. Quim.*, 1933, 31, 99; Amadori, *Atti R. Accad. Lincei*, 1918, 27, I, 131; *Gazzetta*, 1918, 48, II, 42; Aten, *Zeitsch. anorg. Chem.*, 1905, 47, 386; Beckmann, *Zeitsch. physikal. Chem.*, 1897, 22, 609. See also *International Critical Tables*, 1928, 4, 38, 39.

Bismuth, Oxygen and Sulphur.

Numerous compounds of bismuth with oxygen and sulphur have been described. The majority of these are basic salts of uncertain constitution. Certain naturally-occurring minerals may possibly be oxysulphides, such as *karelinite*¹ and *bolivite*,² but the evidence does not appear to be sufficient to decide their true nature. A substance of composition corresponding to $\text{Bi}_2\text{O}_3\text{S}$ has been obtained as a greyish-black powder by the action of dry hydrogen sulphide upon bismuth pentoxide (the latter probably containing tetroxide), and by passing hydrogen sulphide through a suspension of bismuth pentoxide in boiling benzene. It is stable in air up to 120°C ., but when heated above that temperature is converted into bismuth trioxide and sulphur dioxide. It dissolves in hydrochloric acid with evolution of hydrogen sulphide.³

Bismuth Sulphites.—Normal bismuth sulphite has not yet been obtained, but a number of basic compounds have been obtained. They are all white, powdery substances obtained by the action of a solution of bismuth nitrate in nitric acid upon a solution of sodium sulphite. The nature of the product depends upon the temperature and concentration of the solutions.⁴ Among the sulphites that have been described are: $9(\text{BiO})_2\text{SO}_3 \cdot (\text{BiOH})\text{SO}_3 \cdot 2\text{H}_2\text{O}$, $4(\text{BiO})_2\text{SO}_3 \cdot (\text{BiOH})\text{SO}_3 \cdot 5\text{H}_2\text{O}$, $2(\text{BiO})_2\text{SO}_3 \cdot 3(\text{BiOH})\text{SO}_3 \cdot 2\text{H}_2\text{O}$, $3(\text{BiO})_2\text{SO}_3 \cdot 7(\text{BiOH})\text{SO}_3 \cdot 10\text{H}_2\text{O}$, $(\text{BiO})_2\text{SO}_3 \cdot 3(\text{BiOH})\text{SO}_3 \cdot \text{H}_2\text{O}$. By the action of hot sulphurous acid upon bismuth trioxide, a white, powdery compound has been obtained to which is ascribed the formula $(\text{BiO})_2\text{SO}_3 \cdot 2(\text{BiOH})\text{SO}_3 \cdot 4\text{H}_2\text{O}$. It is stable in air, insoluble in water, but slightly soluble in sulphurous acid, from which it may be reprecipitated by dilution.⁵

Bismuth Sulphate.—In addition to the normal sulphate, a number of other compounds, most of which are basic, has been obtained. The products obtained by crystallisation from solutions of bismuth trioxide in sulphuric acid vary in composition according to the temperature and concentration of the solution employed.⁶ From an investigation of the equilibrium of the system $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$, it is found that the solid phase in equilibrium with liquid containing 60 to 90 per cent. of sulphuric acid is $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3$; when the concentration of the liquid phase falls below 47.5 per cent. of sulphuric acid the solid phase in equilibrium is $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$, when the concentration falls below 1.37 per cent. acid the solid phase is a mixture of $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ and $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$, and when the concentration falls below 1.09 per cent. acid $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ alone remains as the solid phase.⁷

Normal bismuth sulphate may be obtained by dissolving bismuth trioxide, bismuth trisulphide or bismuth nitrate in excess of concentrated sulphuric acid, evaporating the solution to dryness and heating the

¹ Rammelsberg, *Mineralchem.*, 1875, 1, 195; Hermann, *J. prakt. Chem.*, 1858, 75, 448; Groth, "*Tabellen*," 4th Ed., p. 49.

² Groth, *loc. cit.*, p. 18; Domeyko, *Compt. rend.*, 1877, 85, 977.

³ Gmelin-Kraut's "*Handbuch der anorganischen Chemie*" (Heidelberg, 1908), Vol. III, Part 2, p. 979.

⁴ Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 72. See also Caglioti and Malossi, *Atti R. Accad. Lincei*, 1929, [6], 10, 97.

⁵ Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 241.

⁶ Adie, *Proc. Chem. Soc.*, 1899, 15, 226.

⁷ Allan, *Amer. Chem. J.*, 1902, 27, 284.

residue very carefully.¹ It is a white, powdery or finely crystalline substance, very hygroscopic, forming a hydrate $\text{Bi}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, which loses water at 100°C ., becoming a dihydrate, $\text{Bi}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$. It can be heated to 400°C . without decomposition, but above that temperature decomposition sets in, basic salts being produced. On strongly heating, $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$ is obtained,² while at red heat all the sulphuric anhydride is driven off.³ It can be reduced to metal by heating in a current of hydrogen⁴ or ammonia.⁵ It is hydrolysed slowly by cold water, more rapidly by hot water, forming in each case $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$. With hydrogen chloride it forms addition compounds,⁷ the following having been obtained: $\text{Bi}_2(\text{SO}_4)_3 \cdot 4\text{HCl}$, $\text{Bi}_2(\text{SO}_4)_3 \cdot 2\text{HCl}$, $\text{Bi}_2(\text{SO}_4)_3 \cdot \text{HCl}$. It forms double salts with the sulphates of the alkali metals and ammonium. With lithium sulphate two compounds have been described,⁸ $\text{Li}_3\text{Bi}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Li}(\text{BiO})\text{SO}_4 \cdot \text{H}_2\text{O}$. With sodium sulphate⁹ the compound $\text{Bi}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4$ has been described; with potassium sulphate¹⁰ the double salt $\text{Bi}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ is obtained in the form of hexagonal crystals; the existence of the compound $\text{Bi}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$, which had previously been described,¹¹ has not been confirmed. The ammonium compound $\text{Bi}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ has also been described.¹² Two compounds with cerium sulphate, $\text{Bi}(\text{OH})\text{SO}_4 \cdot \text{Ce}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ and $2\text{Bi}_2(\text{SO}_4)_3 \cdot \text{Ce}(\text{SO}_4)_2 \cdot 15\text{H}_2\text{O}$, have been described, and solid solutions are also found in this system.¹³

Bismuth sulphate is isomorphous with the sulphates of yttrium, lanthanum and "didymium."¹⁴ It is said to be able to confer upon certain other substances the property of phosphorescence.¹⁵

Acid Bismuth Sulphate, $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$, is obtained by the action of moderately concentrated sulphuric acid upon bismuth trioxide, the basic sulphate first formed being redissolved in a large excess of sulphuric acid.¹⁶

In addition to the foregoing, several other sulphates, both acid and basic, have been described; it is possible that many of them are mixtures of the normal sulphate, bismuth oxide and water. The following may be mentioned: $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3$, $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$,¹⁷ $3\text{Bi}_2\text{O}_3 \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$,¹⁸ $5\text{Bi}_2\text{O}_3 \cdot 11\text{SO}_3 \cdot 17\text{H}_2\text{O}$, $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 8\text{H}_2\text{O}$, $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$, $\text{Bi}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 10\text{H}_2\text{O}$.¹⁹

¹ Lagerhjelm, *Schweigger's J.*, 1817, 17, 416; Leist, *Annalen*, 1871, 160, 29; Schultz-Sellaack, *Ber.*, 1871, 4, 13; Marignac, *Ann. Chim. Phys.*, 1884, [6], 1, 294; *J. prakt. Chem.*, 1884, [2], 30, 244; Hensgen, *Rec. Trav. chim.*, 1885, 4, 409; Bailey, *J. Chem. Soc.*, 1887, 51, 679; Classen, *J. prakt. Chem.*, 1891, [2], 43, 133.

² Heintz, *Pogg. Annalen*, 1844, 63, 77.

³ Bailey, *loc. cit.*; Schmidt, *Ber.*, 1894, 27, 236.

⁴ Arfvedson, *Pogg. Annalen*, 1824, 1, 74.

⁵ Hodgkinson and Trench, *Chem. News*, 1892, 66, 223.

⁶ Hensgen, *loc. cit.*

⁷ Ephraim, *Ber.*, 1926, 59 B, 790; Hensgen, *loc. cit.*

⁸ Malossi, *Atti R. Accad. Lincei*, 1931, [6], 13, 775.

⁹ Lüddecke, *Annalen*, 1866, 140, 277.

¹⁰ Caglioti and Stolfi, *Atti R. Accad. Lincei*, 1927, [6], 5, 896.

¹¹ Remsen, *Amer. Chem. J.*, 1892, 14, 81.

¹² Lüddecke, *Annalen*, 1866, 140, 277. See, however, Caglioti and Malossi, *Atti R. Accad. Lincei*, 1929, [6], 10, 97.

¹³ Cattica and Bonamini, *Gazzetta*, 1923, 53, 761.

¹⁴ Bodman, *Zeitsch. anorg. Chem.*, 1901, 27, 254.

¹⁵ de Boisbaudran, *Compt. rend.*, 1886, 103, 629, 1064; 1887, 104, 1680; 1887, 105, 45, 206.

¹⁶ Leist, *loc. cit.*; Adie, *loc. cit.*; Allan, *loc. cit.*

¹⁷ Heintz, *Pogg. Annalen*, 1844, 63, 55.

¹⁸ Athanasesco, *Compt. rend.*, 1886, 103, 271.

¹⁹ Adie, *loc. cit.*

Bismuth Thiosulphates.—Bismuth thiosulphate itself has not yet been prepared. Addition of a thiosulphate to a bismuth solution results in the precipitation of bismuth trisulphide, a reaction which has been recommended for the separation and detection of bismuth.¹ Several complex compounds containing bismuth and alkali or alkaline earth thiosulphates have been described, however; solutions of these are in general acid, and do not respond to the usual reactions for thiosulphates unless they are made neutral;² it is suggested that they contain an unstable anion $\text{Bi}(\text{S}_2\text{O}_3)_3^-$.

Sodium Bismuth Thiosulphate, $\text{Na}_3\text{Bi}(\text{S}_2\text{O}_3)_3$, is obtained in the form of orange-yellow crystals when bismuth nitrate is rubbed with excess of sodium thiosulphate. The mixture is extracted with aqueous alcohol, and the compound precipitated as a yellow oil by addition of more alcohol, crystals being obtained by drying over sulphuric acid.³ A solution of this salt has been suggested as a reagent for the detection and estimation of potassium,⁴ but has been found unsatisfactory for the purpose, as the potassium salt precipitated is always contaminated with the sodium salt.⁵ A crystalline precipitate of sodium bismuth thiosulphate has also been obtained by the action of aniline and alcohol on a solution containing bismuth oxynitrate, acetic acid and sodium thiosulphate.⁶ By the interaction of a solution of bismuth nitrate in mannitol⁷ and sodium thiosulphate in the presence of manganese chloride a compound, more stable than that described by Hauser, has been obtained in the form of small octahedra⁸ to which the formula $\text{Na}_3\text{Bi}(\text{S}_2\text{O}_3)_3$ has been ascribed.

Potassium Bismuth Thiosulphate, $\text{K}_3\text{Bi}(\text{S}_2\text{O}_3)_3$, is obtained by precipitation from a solution of the sodium salt on adding a potassium salt and alcohol,⁹ or by the addition of solutions of potassium chloride and sodium thiosulphate to one of bismuth trioxide in hydrochloric acid.¹⁰ It may be obtained in the anhydrous and hydrated forms. The corresponding salts of *rubidium* and *cæsium*, $\text{Rb}_3\text{Bi}(\text{S}_2\text{O}_3)_3$ and $\text{Cs}_3\text{Bi}(\text{S}_2\text{O}_3)_3$, both of which are yellow, crystalline powders, *ammonium*, $(\text{NH}_4)_3\text{Bi}(\text{S}_2\text{O}_3)_3$, *strontium*, $\text{Sr}_3[\text{Bi}(\text{S}_2\text{O}_3)_3]_2$, *barium*, $\text{Ba}_3[\text{Bi}(\text{S}_2\text{O}_3)_3]_2$, *silver* and *copper* have been prepared in a similar manner.¹¹ The barium and strontium salts are readily hydrolysed by water, the silver salt decomposes in a few seconds with the formation of a black compound, while the copper salt is precipitated only on the addition of alcohol.

By the interaction of the double thiosulphate of sodium and thallium with bismuth trichloride, a *thallium bismuth thiosulphate*, $\text{Tl}_3\text{Bi}(\text{S}_2\text{O}_3)_3$, is obtained. It may also be prepared by the interaction of a thalious salt with potassium bismuthothiosulphate, but it is soluble in excess of the latter.¹² It is a sparingly soluble, microcrystalline yellow powder. Although moderately stable in neutral solutions, it is readily decomposed

¹ Vortmann, *Monatsh.*, 1886, 7, 418; Faktor, *Pharm. Post*, 1900, 33, 301, 317.

² Hauser, *Zeitsch. anorg. Chem.*, 1903, 35, 1; Cuisinier, *Bull. Soc. chim.*, 1922, 31, 1064.

³ Hauser, *loc. cit.*

⁴ Carnot, *Compt. rend.*, 1876, 83, 338, 390; 1877, 84, 1504; 1878, 86, 478.

⁵ Küster and Grütters, *Zeitsch. anorg. Chem.*, 1903, 36, 325; Cuisinier, *loc. cit.*

⁶ Sanchez, *Bull. Soc. chim.*, 1912, [iv], 11, 440. See also Cuisinier, *loc. cit.*

⁷ Vanino and Hauser, *Zeitsch. anorg. Chem.*, 1901, 28, 210.

⁸ Vanino and Musgnug, *Arch. Pharm.*, 1919, 257, 264.

⁹ Carnot, *Compt. rend.*, 1876, 83, 338, 390.

¹⁰ Hauser, *loc. cit.*

¹¹ Vanino and Musgnug, *loc. cit.*

¹² Canneri, *Gazzetta*, 1922, 52, 37.

by acids with evolution of sulphur dioxide and precipitation of bismuth trisulphide, the latter being quantitative.

Attempts to obtain bismuth dithionate and bismuth trithionate have proved unsuccessful.¹

BISMUTH AND SELENIUM.

Three compounds of bismuth and selenium have been reported, Bi_2Se , BiSe and Bi_2Se_3 . Of these BiSe and Bi_2Se_3 are probably true compounds,² the latter being the more stable. Octahedral crystals of **bismuth subselenide**, Bi_2Se_3 , are stated to be formed when selenium is melted with a large excess of bismuth.³ The existence of this compound, however, has not been confirmed. The melting point curve of the system Bi-Se indicates the formation of the **monoselenide**, BiSe , which decomposes at 602°C . (see fig. 10, p. 195). This compound is dimorphous, with a transition point at 422°C . On heating bismuth with excess of selenium, the **triselenide**, Bi_2Se_3 , is formed.⁴ The mineral *silaonite*, found in Mexico, to which the formula Bi_2Se_3 was formerly given,⁵ is more probably a mixture of the triselenide Bi_2Se_3 with bismuth.⁶

Bismuth Triselenide is found in the minerals *guanajuatite* and *frenzelite*. It may be obtained by melting together the elements, but on account of the ease with which selenium volatilises, to obtain the pure compound it is necessary to add more selenium to the product first formed and remelt in the absence of air.⁷ It is formed when hydrogen selenide is passed into a solution of bismuth nitrate from which excess acid has been almost completely removed,⁸ or by the addition of a solution of a bismuth salt to a saturated solution of hydrogen selenide. The hydrogen selenide is best prepared by the action of hydrochloric acid on magnesium selenide in the absence of air. It is probable that by the last-mentioned process bismuth selenide is obtained free from deposited metal and from complexes.⁹

In the mineral form bismuth triselenide is isomorphous with the minerals bismuthinite and antimonite.¹⁰ Its hardness on Mohs' scale is 2.5 to 3.5, and its density 6.2 to 6.6; it is commonly associated with sulphur minerals, and indeed sulphur may partially replace selenium. In the prepared form it is a black or grey powder with a density of 6.82. When heated it loses selenium and absorbs oxygen. It is only very slightly attacked by concentrated hydrochloric acid even on boiling; dilute nitric acid has little action, but concentrated nitric acid and aqua regia decompose it completely with partial separation of selenium. It is insoluble in solutions of potassium hydroxide or potassium sulphide. It is oxidised to the trioxide when fused with potassium nitrate, potassium selenate being formed at the same time. It reacts with the

¹ Vanino and Mussgnug, *loc. cit.*

² Parravano and Caghoti, *Gazzetta*, 1930, 60, 923.

³ Rössler, *Zeitsch. anorg. Chem.*, 1895, 9, 46, 50.

⁴ Pélabon, *J. Chim. phys.*, 1904, 2, 321; Parravano, *Gazzetta*, 1913, 43, I, 210; Tomoshige, *Mem. Coll. Sci. Kyōto*, 1919, 4, 57. See also *International Critical Tables*, 1928, 4, 26.

⁵ Mallet, *Jahrb. Miner.*, 1880, 160.

⁶ Bruns, *Zeitsch. Kryst. Min.*, 1882, 6, 96.

⁷ Schneider, *Pogg. Annalen*, 1855, 94, 628; Little, *Annalen*, 1859, 112, 213.

⁸ Uelsmann, *Annalen*, 1860, 116, 125.

⁹ Moser and Atynski, *Monatsh.*, 1925, 45, 235.

¹⁰ Schrauf, *Jahrb. Miner.*, 1875, 685.

double chloride of bismuth and ammonium when melted, with formation of **bismuth selenochloride**, BiSeCl .

Thermal investigation of the system $\text{Bi}_2\text{S}_3\text{-Ag}_2\text{Se}$ has been undertaken,¹ and from the melting point curve it is deduced that a double compound $3\text{Ag}_2\text{Se} \cdot 4\text{Bi}_2\text{S}_3$ is obtained, the melting point being 773°C . (see fig. 11, p. 200).

Two **selenites** of bismuth have been described, the first, $\text{Bi}_2\text{O}_3 \cdot 4\text{SeO}_2$, being formed by the addition of selenious acid to bismuth carbonate, and the second, $\text{Bi}_2\text{O}_3 \cdot 5\text{SeO}_2 \cdot \text{H}_2\text{O}$, by the action of excess of selenious acid upon bismuth hydroxide.²

A compound which may be **bismuth selenate** is obtained in the form of very small, colourless prisms by boiling bismuth carbonate with excess of selenic acid and removing the excess acid by heating.³ It is insoluble in water and is not decomposed by boiling water; it dissolves in mineral acids, but is decomposed by alkalis. The existence of selenites and selenates of bismuth has not, however, been confirmed.

BISMUTH AND TELLURIUM.

By the action of hydrogen telluride or sodium telluride upon a salt of bismuth, a **monotelluride**, BiTe , has been obtained,⁴ which is described as being unstable in air, as having reducing properties and as being soluble in acids. No evidence for the existence of this compound has, however, been obtained from thermal (see fig. 10, p. 195) and microscopic examinations of the system Bi-Te , **bismuth tritelluride**, Bi_2Te_3 , being the only definite compound of the two elements indicated.⁵ Bismuth telluride occurs in certain minerals, while a **thiotelluride**, $\text{Bi}_2\text{Te}_2\text{S}$, occurs as tetradymite. It is probable that the mineral montanite⁶ contains a **bismuth tellurate**, $(\text{BiO})_2\text{TeO}_4$, in a hydrated form. No compound of this type appears, however, to have been obtained artificially.

Compounds described as thiotellurites, of doubtful composition, were mentioned by Berzelius.⁷ Such compounds do not appear to have been examined subsequently.

BISMUTH AND CHROMIUM.

Bismuth Chromite, $3\text{Bi}_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$, is prepared by heating bismuth oxychloride with chromium trioxide and water for several hours.⁸ It is a brown powder which is insoluble in water, in acids (including aqua regia) and in alkalis.

Many **chromates** and **dichromates** of bismuth have from time to time been described,⁹ but all except two are probably mixtures. These

¹ Pélabon, *Compt. rend.*, 1908, 146, 975.

² Nilson, *Bull. Soc. chim.*, 1875, [2], 23, 498.

³ Cameron and MacAllan, *Proc. Roy. Soc.*, 1889, 46, 13.

⁴ Brukl, *Monatsh.*, 1925, 45, 471.

⁵ Monkemeyer, *Zeitsch. anorg. Chem.*, 1905, 46, 415; Pélabon, *Ann. Chim. Phys.*, 1909, 17, 526; Amadori, *Atti R. Accad. Lincei*, 1918, 27, I, 131; *Gazzetta*, 1918, 48, II, 42; Endo, *Sci. Rep. Tohoku Imp. Univ.*, 1925, 14, 479; 1927, 16, 201. See also *International Critical Tables*, 1928, 4, 28.

⁶ Genth, *Amer. J. Sci.*, 1868, [2], 45, 306.

⁷ Berzelius, "*Lehrbuch*," 1826.

⁸ Briggs, *J. Chem. Soc.*, 1929, 132, 242.

⁹ Löwe, *J. prakt. Chem.*, 1856, 67, 288, 463; Pearson, *Phil. Mag.*, 1856, [4], 11, 204; Muir, *J. Chem. Soc.*, 1876, 30, 15; 1877, 31, 24; Schmid, *Inaug. Dissertation Erlangen*, 1891. See also Briggs, *loc. cit.*

two compounds may be obtained by the action of chromic acid upon bismuth trioxide. If the concentration of the acid exceeds 7·8 moles per litre the substance $\text{Bi}_2\text{O}_3 \cdot 4\text{CrO}_3$ is obtained as a stable salt; if the concentration falls below that figure, this salt is hydrolysed and the substance $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ is obtained.¹ The former is an orange-scarlet powder and is perhaps a mixed dichromate and chromate, $\text{Bi}_2\text{Cr}_2\text{O}_7(\text{CrO}_4)_2$; the latter is a basic salt, and is obtained as an orange-yellow powder. It may also be prepared by the action of potassium chromate or dichromate on a nearly neutral solution of bismuth nitrate.²

Several double chromates with alkali compounds have also been described.³

BISMUTH AND MOLYBDENUM, ETC.

Bismuth compounds react with molybdates, phosphomolybdates and tungstates to form insoluble substances.⁴

BISMUTH AND NITROGEN.

Bismuth Nitride, BiN .—When potassamide is added to a solution of bismuth tribromide or triiodide in liquid ammonia, a dark brown precipitate of bismuth nitride, BiN , is formed; it is very unstable, decomposing explosively when acted on by water, or when heated.⁵ It has been used as a nitriding agent.⁶

Bismuthyl Nitrite, or Basic Bismuth Nitrite, $2\text{BiONO}_2 \cdot \text{H}_2\text{O}$, is obtained as a yellowish-white precipitate when sodium nitrite is added to an aqueous solution of normal bismuth nitrate and mannitol. The anhydrous salt can be obtained by drying over sulphuric acid in a vacuum desiccator.⁷ The salt decomposes when heated above 60°C ., with evolution of nitrogen tetroxide.

Although attempts to prepare pure normal bismuth nitrite have not proved successful, a number of complex nitrites, or **bismuthinitrites**, have been obtained.⁸ They may be prepared by precipitation from a strong solution of alkali nitrite by bismuth nitrate or a mixture of the nitrates of a third metal and bismuth. Two groups of salts have been prepared, the simple bismuthinitrites, for which the general formula is $\text{M}_3\text{Bi}(\text{NO}_2)_6$, and the mixed bismuthinitrites, having a general formula $\text{M}_2\text{M}'\text{Bi}(\text{NO}_2)_6$, where M represents ammonium, potassium, rubidium, caesium or thallium, and M' represents one of the three metals lithium, sodium or silver. All possible compounds of the first type, except that of ammonium, have been obtained, as also have all possible compounds of the second type. All the salts are highly crystalline, the simple type forming orange or yellow hexagonal plates, but the mixed type pale yellow to red crystals, probably octahedral. The simple bismuthinitrites of caesium and thallium differ somewhat in constitution from the normal type, the *caesium* compound, $\text{Cs}_3\text{Bi}(\text{NO}_2)_6 \cdot \text{Bi}(\text{NO}_2)_3$, containing an additional molecule of bismuth nitrite, while that of *thallium*,

¹ Cox, *Zeitsch. anorg. Chem.*, 1906, 50, 226.

² Muir, *loc. cit.*

³ See this Series, Vol. VII, Part III, p. 48.

⁴ Gaspar y Arnal, *Ann. Chim. appl.*, 1929, 11, 97. For the molybdates, tungstates and uranates of bismuth, see this Series, Vol. VII, Part III, pp. 140, 215, 308.

⁵ Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 820.

⁶ Schurman and Fernelius, *ibid.*, 1930, 52, 2425.

⁷ Vanino and Hartl, *J. prakt. Chem.*, 1906, [2], 74, 150.

⁸ Ball, *J. Chem. Soc.*, 1905, 87, 761.

$\text{Ti}_3\text{Bi}(\text{NO}_2)_6 \cdot \text{TiNO}_2 \cdot \text{H}_2\text{O}$, contains an additional molecule of thallose nitrite.¹ All compounds that have been prepared are readily hydrolysed by water; the simple bismuthinitrites are generally less stable and more soluble than the mixed salts. Attempts to prepare compounds containing two metals of the M group, or two of the M' group, have proved unsuccessful; so also have attempts to prepare salts of the type $\text{M}'_3\text{Bi}(\text{NO}_2)_6$, thus, sodium bismuthinitrite has not been obtained in the solid form, but is probably produced in solution when bismuth nitrate is added to a solution of sodium nitrite. The reagent prepared in this way has been suggested for use in the detection and separation of rubidium and caesium, while the solution obtained by adding the nitrates of bismuth and caesium to a solution of potassium nitrite has been used for the estimation of sodium, owing to the formation of *sodium caesium bismuthinitrite*, which is soluble only with difficulty. This substance, however, appears to vary in composition according to the method of preparation.²

In addition, a number of bismuthinitrites containing nickel have been prepared by the addition of a salt of any of the metals of the M group to a solution containing nickel nitrate, bismuth nitrate, and sodium or lithium nitrite.³ The composition of these compounds has not in all cases been definitely established.

By the addition of a saturated solution of bismuth nitrate, in varying proportions, to a saturated solution of sodium cobaltinitrite, three distinct *bismuth oxycobaltinitrites*, or *bismuthyl cobaltinitrites*, have been obtained,⁴ ranging in colour from brick-red to yellow and having the compositions $(\text{BiO})_3\text{Co}(\text{NO}_2)_6$, $(\text{BiO})_3\text{Co}(\text{NO}_2)_5$, and $(\text{BiO})_3\text{Co}(\text{NO}_2)_4$, respectively. These compounds are all very hygroscopic. They are decomposed by water on standing, are readily decomposed by acids with evolution of nitrogen peroxide, and by solutions of sodium and ammonium hydroxides. They are insoluble in ether and only slightly soluble in alcohol. The following co-ordination formulæ have been suggested: $[\text{Co}(\text{NO}_2)_6]_3\text{BiO}$, $[\text{Co}(\text{NO}_2)_5(\text{BiO})]_2\text{BiO}$, and $[\text{Co}(\text{NO}_2)_4(\text{BiO})_2]\text{BiO}$.

Normal Bismuth Nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, is obtained by dissolving powdered bismuth in nitric acid; on crystallising from solution, large, prismatic, triclinic crystals having the elements

$$a : b : c = 0.8053 : 1 : 0.6172 ; \alpha = 90^\circ 4' ; \beta = 104^\circ 26' ; \gamma = 79^\circ 6'$$

are formed,⁵ being isomorphous with those of the corresponding but labile nitrates of the rare earth metals neodymium and praseodymium.⁶ Its density is 2.7 to 2.8.⁷ On exposure to dry air at the ordinary temperature the nitrate disintegrates and is gradually converted into a basic nitrate.⁸ It cannot be dehydrated completely by phosphorus pentoxide, as decomposition sets in.⁹ The action of heat on the normal salt is extremely complex, and the results obtained by different investigators

¹ Ball and Abram, *J. Chem. Soc.*, 1913, 103, 2110.

² Ball, *J. Chem. Soc.*, 1909, 95, 2126; 1910, 97, 1408.

³ Ball and Abram, *loc. cit.*, p. 2126.

⁴ Ogburn, *J. Amer. Chem. Soc.*, 1923, 45, 641.

⁵ Rammelsberg, *Handbuch*, 1881, I, 366.

⁶ Bodman, *Ber.*, 1898, 31, 1237; *Zeitsch. anorg. Chem.*, 1901, 27, 254; Urban and Lacombe, *J. Chim. phys.*, 1906, 4, 105; Friend, *J. Chem. Soc.*, 1935, 138, 824, 1431.

⁷ Playfair and Joule, *Memoirs Chem. Soc.*, 1845, 2, 401; Clarke, *Amer. J. Sci.*, 1877, [3], 14, 281.

⁸ Ruge, *J. prakt. Chem.*, 1865, 96, 117.

⁹ Picon, *Bull. Soc. chim.*, 1925, 37, 1365; *Compt. rend.*, 1925, 181, 516.

are conflicting.¹ Rutten² observed that at 72° C. a little liquid is formed, but that maintaining the mass at that temperature does not produce more liquid. The remaining crystals, freed from liquid, melt at 75·5° C., giving basic salt and liquid. The trioxide results at 425° C.³ Earlier workers, however, stated that the anhydrous oxide was formed at as low a temperature as 260° C. The first product of decomposition appears to be the basic nitrate, $2\text{BiONO}_3 \cdot \text{H}_2\text{O}$, but several other products have been reported.

Bismuth nitrate is soluble in water, but excess of water must be avoided; the solution, which is acid in consequence of hydrolysis, rapidly decomposes⁴ with the formation of oxynitrate, BiONO_3 . It is soluble in nitric acid, and the refractive power of the solution has been studied.⁵ It is insoluble in anhydrous hydrofluoric acid,⁶ but readily soluble in an aqueous solution of mannitol,⁷ forming a clear solution which probably contains complex compounds.⁸ This solution may be employed for the preparation of many bismuth salts.

The *sesquihydrate*, $2\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, is obtained by treating Bi_2O_3 or the normal pentahydrated salt with fuming nitric acid. It is very deliquescent.⁹ A *dihydrate*, $\text{Bi}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, has also been prepared.

Many **double nitrates** have been obtained¹⁰ of the type $3\text{M}(\text{NO}_3)_2 \cdot 2\text{Bi}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$, in which M represents magnesium, zinc, nickel, cobalt or manganese. They are prepared by dissolving the simple nitrates in the smallest quantity of hot, fairly concentrated nitric acid, and allowing the solution to crystallise. These double salts are isomorphous with the similar double nitrates obtained by substituting metals of the rare earths for bismuth. They are all decomposed by water. *Magnesium bismuth nitrate*, $\text{Mg}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, is colourless; its density is 2·32, and it melts with decomposition at 71° C. *Zinc bismuth nitrate*, $\text{Zn}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, is colourless; its density is 2·75, and it melts with decomposition at 67·5° C. *Nickel bismuth nitrate*, $\text{Ni}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, is green; its density is 2·51, and it melts without decomposition at 69° C. *Cobalt bismuth nitrate*, $\text{Co}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, is orange-red; its density is 2·48, and it melts without decomposition at 58° C. *Manganese bismuth nitrate*, $\text{Mn}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, is pale red; its density is 2·42, and it melts without decomposition at 43° to 44° C. In addition, *mercury bismuth nitrate*, $\text{Hg}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, has been obtained;¹¹ it forms solid solutions with magnesium bismuth nitrate containing up to 25 per cent. of the mercury salt. Magnesium bismuth nitrate has been employed for the separation of the metals of the rare earths.¹²

From an examination of the behaviour of normal bismuth nitrate,

¹ Berzelius, *Gilbert's Annalen*, 1812, 40, 286; Gladstone, *J. prakt. Chem.*, 1835, 44, 179; Graham, *Annalen*, 1839, 29, 16; Yvon, *Compt. rend.*, 1877, 84, 1161; Bito, Aoyama and Matsui, *J. Soc. Chem. Ind., Japan*, 1932, 35, 195. For more complete bibliography and discussion, see Picon, *loc. cit.*

² Rutten, *Zeitsch. anorg. Chem.*, 1902, 30, 342.

³ Picon, *loc. cit.*

⁴ Grouvelle, *Ann. Chim. Phys.*, 1821, [2], 19, 141; Duflos, *Schweigger's J.*, 1833, 68, 19; Antoni and Gigli, *Gazzetta*, 1898, 28, 248.

⁵ Baden-Powell, *Pogg. Annalen*, 1846, 69, 110; Ditscheiner, *Sitzungsber. K. Akad. Wiss. Wien*, 1864, 49, 326.

⁶ Fredenhagen and Cadenbach, *Zeitsch. physikal. Chem.*, 1930, A 146, 245.

⁷ Vanino and Hartl, *Zeitsch. anorg. Chem.*, 1901, 28, 201.

⁸ De Carli, *Ann. Chim. applicata*, 1931, 21, 472.

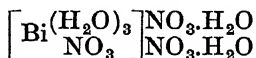
⁹ Rutten, *loc. cit.*

¹⁰ Urbain and Lacombe, *Compt. rend.*, 1903, 137, 568.

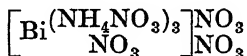
¹¹ Carobbi and Marcolongo, *Gazzetta*, 1926, 56, 69.

¹² Urbain and Lacombe, *Compt. rend.*, 1904, 138, 84.

and of compounds of this salt with certain sugars and other organic substances,¹ it has been suggested that the co-ordination formula should be



From a solution of bismuth nitrate in aqueous ammonium nitrate there is obtained by crystallisation a double compound which may be represented by



Basic Bismuth Nitrate.—The earliest investigators were well aware that bismuth nitrate is decomposed by water; indeed a cosmetic known as "Spanish White" was prepared in this way.² Many substances have been described as resulting from the hydrolysis of bismuth nitrate, but there can be little doubt that many of these are mixtures. The composition of the product obtained depends upon a number of factors, such as the quantity and temperature of the water employed, the time that the precipitated substance stands in contact with the liquid, the process of washing, etc.³

The system $\text{Bi}_2\text{O}_3\text{--N}_2\text{O}_5\text{--H}_2\text{O}$ has been systematically investigated,⁴ and the various compounds produced by hydrolysis have been examined by analysis and by titrimetric measurements, and from the results co-ordination formulæ have been given.⁵ The first product obtained by the action of cold water, or very dilute nitric acid, upon normal hydrated bismuth nitrate is the compound $\text{Bi}_2\text{O}_3\text{.N}_2\text{O}_5\text{.2H}_2\text{O}$, or $\text{BiONO}_3\text{.H}_2\text{O}$, which forms very thin crystalline plates showing double refraction. When this body is treated with a little warm water, or when it is allowed to stand in contact with liquid containing not more than six per cent. of nitrogen pentoxide, monoclinic crystals of the basic salt $\text{Bi}_2\text{O}_3\text{.N}_2\text{O}_5\text{.H}_2\text{O}$ or $[\text{BiO}(\text{NO}_3)\text{.Bi}(\text{OH})_2]\text{NO}_3$ are formed. This compound may also be obtained in the form of thin hexagonal prisms by the action of heat upon the hydrated normal nitrate, which decomposes at about 72°C . Its solubility in water falls with rise of temperature. When the compound $\text{BiONO}_3\text{.H}_2\text{O}$ is allowed to stand in contact with very dilute solution, or when the normal nitrate is decomposed by a large excess of water, rhombic crystals of a complex compound $6\text{Bi}_2\text{O}_3\text{.5N}_2\text{O}_5\text{.9(8)H}_2\text{O}$ or $\left[\text{Bi}_2\text{O}(\text{OH})_3\text{NO}_3 \right]_2 \{ \text{Bi}_2\text{O}(\text{OH})_2\text{NO}_3 \} \left[\text{NO}_3 \right]_2$ are obtained. The same compound is obtained in the form of hexagonal plates when the basic compound $\text{Bi}_2\text{O}_3\text{.N}_2\text{O}_5\text{.H}_2\text{O}$ is acted upon by excess of warm water. The final product obtained by hydrolysis, using boiling

¹ Hepner and Likiernik, *Arch. Pharm.*, 1926, 264, 46.

² Kopp, "*Geschichte der Chemie*" (Braunschweig, 1847), Vol. IV, p. 110.

³ Schamelhaut, *J. Pharm. Belge.*, 1929, 11, 21; Herberger, *Repertorium für die Pharmacie*, 1836, 55, 289, 306; Ullgren, *Berzelius Jahresberichte*, 1839, 17, 169; Duflos, *Arch. Pharm.*, 1840, [2], 23, 307; Heintz, *J. prakt. Chem.*, 1848, 45, 102; Gladstone, *Memoirs Chem. Soc.*, 1845–1847, 3, 480; *J. prakt. Chem.*, 1848, 44, 179; Becker, *Arch. Pharm.*, 1848, [2], 55, 1, 129; 1854, [2], 79, 1; Janssen, *Arch. Pharm.*, 1851, [2], 68, 1, 129; Dulk, *Repertorium für die Pharmacie*, 1844, [2], 33, 1; Lüddecke, *Annalen*, 1866, 140, 227; Ditte, *Compt. rend.*, 1874, 79, 956; Rousseau and Tite, *Compt. rend.*, 1892, 115, 174; Yvon, *Bull. Soc. chim.*, 1877, 1, 491.

⁴ van Bemmelen and Rutten, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 196; Rutten, *Zeitsch. anorg. Chem.*, 1902, 30, 342. See also Ditte, *Ber.*, 1874, 7, 1644; Allan, *J. Amer. Chem. Soc.*, 1903, 25, 307.

⁵ Hepner, *Arch. Pharm.*, 1926, 264, 55.

water, is $2\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ or $\text{BiO}(\text{NO}_3) \cdot \text{BiO}(\text{OH})$, which forms hexagonal crystals.

By precipitation from solutions of bismuth nitrate with ammonium hydroxide, the basic nitrate $(\text{Bi}_2\text{O}_3)_2 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ is obtained.¹ Similarly the basic nitrates $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$ and $2\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$ are obtained by the action of sodium acetate upon solutions of bismuth nitrate.²

From measurements of electrical conductivity it has been shown that hydrolysis of bismuth nitrate occurs even in the presence of excess of

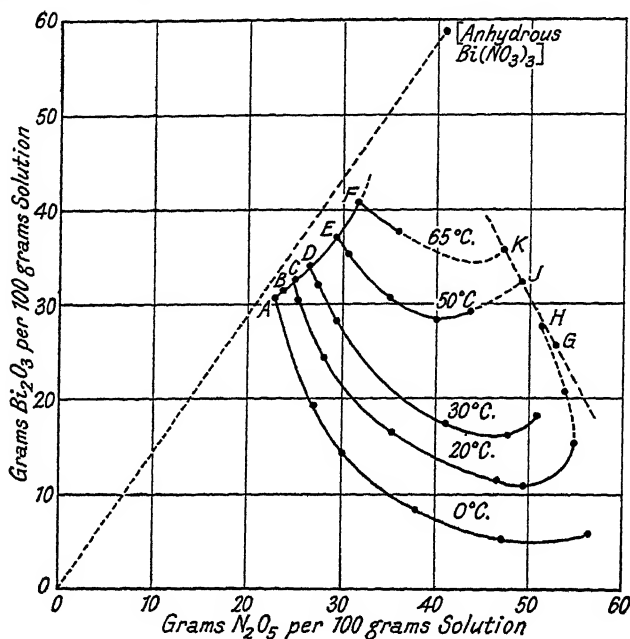


FIG. 12.—Solubility of Bismuth Nitrate in Various Concentrations of Nitric Acid.

nitric acid;³ from these measurements it is also deduced that the compound $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ is not produced directly, but that an intermediate compound, which may perhaps be $\text{BiOH}(\text{NO}_3)_2$, is formed first. This compound does not appear to have been isolated.

Basic bismuth nitrate combines with certain sugars to form compounds in which the NO_3 group is not ionised.⁴

In addition to the above-mentioned substances, two other basic compounds have been obtained, $\text{Bi}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ and $10\text{Bi}_2\text{O}_3 \cdot 9\text{N}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$. Other basic salts mentioned in the literature would appear to be mixtures.⁵

In the following tables are given the solubilities of the basic and normal nitrates of bismuth at different temperatures in various concentrations of nitric acid. The solubilities are expressed as grams of Bi_2O_3 and N_2O_5 respectively per 100 grams of solution.

¹ Hackspill and Kieffer, *Ann. Chim.*, 1930, [10], 14, 227.

² Kharmandaryan, *J. Russ. Phys. Chem. Soc.*, 1928, 60, 1477.

³ Quartaroli, *Gazzetta*, 1913, 43, 1, 97.

⁴ Hepner and Likiernik, *Arch. Pharm.*, 1926, 264, 46.

⁵ van Bemmelen and Rutten, *loc. cit.*; Rutten, *loc. cit.*

SOLUBILITIES OF BASIC BISMUTH NITRATES.

Temp., °C.	Solid Phase.	Bi ₂ O ₃ .	N ₂ O ₅ .	Authority.
20	Bi ₂ O ₃ .N ₂ O ₅ .H ₂ O	Grams.	Grams.	Rutten, <i>Zeitsch. anorg. Chem.</i> , 1902, 30, 342.
		18.67	12.50	
		14.85	13.81	
		18.74	15.90	
		23.50 *	19.25 *	
		27.15	20.96	
		28.11	21.64	
		29.50	22.53	
		30.19	22.90	
		31.48	23.70	
25	Bi ₂ O ₃ .N ₂ O ₅ .2H ₂ O	0.063	0.554	Smith, <i>J. Amer. Chem. Soc.</i> , 1923, 45, 360.
		0.335	1.163	
		1.126	2.368	
		2.23	3.61	
		3.49	4.84	
		5.03	6.21	
65	Bi ₂ O ₃ .N ₂ O ₅ .H ₂ O	5.55	7.44	Rutten, <i>loc. cit.</i>
		26.72	22.46	

* Mean of two separate experiments.

SOLUBILITIES OF BISMUTH NITRATE PENTA-HYDRATE, Bi(NO₃)₃.5H₂O.

Temp., °C.	Bi ₂ O ₃ .	N ₂ O ₅ .	Authority.	Temp., °C.	Bi ₂ O ₃ .	N ₂ O ₅ .	Authority.
0	Grams.	Grams.	F. and H.*	30	Grams.	Grams.	F. and H. Rutten. F. and H. Rutten. F. and H.
	19.71	27.11			32.13	27.15	
	14.17	30.03			28.20	29.60	
	8.57	38.02			17.50	41.10	
	5.30	47.17			16.10	47.70	
	5.92	56.37			18.18	50.67	
20	32.97 †	24.85 †	Rutten.	50	35.63	30.76	F. and H.
	32.63 †	24.65 †			30.85	35.06	
	32.24	24.68			28.21	40.00	
	30.29 †	25.22 †			29.79	43.69	
	24.16	28.25					
	16.62	35.40		65	37.82	35.80	Rutten.
	12.17	43.37					
	11.66	46.62					
	11.19	49.79 †					
	15.20	54.66					
	20.76	53.75					

* Friend and Hall, Private communication.

† Mean of two separate experiments.

The results contained in this second table are shown diagrammatically in fig. 12.

SOLUBILITIES OF BISMUTH NITRATE SESQUI-HYDRATE, $2\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$.

(Rutten.)

At 20° C.	Bi_2O_3 . . .	8.58 grams	4.05 grams
	N_2O_5 . . .	68.28 „	74.90 „
At 65° C.	Bi_2O_3 . . .	4.59 „	
	N_2O_5 . . .	77.90 „	

The quadruple points corresponding to the coexistence in equilibrium of the phases $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ – $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ –Solution–Vapour, at various temperatures, are as follows :

BASIC QUADRUPLE POINTS.

Point in Fig. 12.	Temp., ° C.	Bi_2O_3 .	N_2O_5 .	Authority.
		Grams.	Grams.	
A	0	30.8	22.8	Friend and Hall.
B	9	31.1	23.85	Rutten.
C	20	32.97	24.85	„
D	30	34.2	26.5	„
E	50	36.9	28.9	„
E	50	37.7	29.0	Friend and Hall.
F	65	40.8	31.6	Rutten.

These points appear to be fairly well established, some of them having been obtained by extrapolation from a considerable number of solubility data.

The following quadruple points are given by Rutten and correspond to the coexistence in equilibrium of the following phases : $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ – $2\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ –Solution–Vapour. These points are open to criticism in that the data from which they were derived appear somewhat scanty. For this reason the curves connecting Rutten's data in these regions are shown as broken lines in fig. 12.

ACID QUADRUPLE POINTS.

(Rutten, *loc. cit.*)

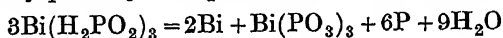
Point in Fig. 12.	Temp., ° C.	Bi_2O_3 .	N_2O_5 .
		Grams.	Grams.
G	11.5	25.36	52.57
H	20.0	27.85	51.02
J	50	32.22	49.29
K	65	35.73	47.02

The conditions of equilibria above 65° C. are very uncertain, for the dihydrate, $\text{Bi}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, appears, and the experimental difficulties are considerable.

BISMUTH AND PHOSPHORUS.

Bismuth Phosphide.—No definite compound of bismuth and phosphorus appears to have been obtained in a pure condition. It has been suggested that a small quantity of the monophosphide, BiP , may be formed when the two elements are melted together,¹ and that this is also formed as a black substance when dry phosphine acts upon bismuth trichloride,² or when phosphine is passed into a solution of bismuth nitrate.³ It is completely decomposed when heated.

Bismuth Hypophosphite, $\text{Bi}(\text{H}_2\text{PO}_2)_3 \cdot \text{H}_2\text{O}$, is obtained as a white crystalline powder by the action of potassium or barium hypophosphite upon a solution of bismuth nitrate.⁴ It is decomposed very readily by heat, phosphine being evolved at temperatures a little above 100° C. At higher temperatures some metallic bismuth is formed, and the reaction may possibly be represented by the equation



It is also readily decomposed by water.⁵

The use of bismuth hypophosphite in conjunction with hydrogen peroxide has been suggested for the quantitative separation of bismuth from other metals.⁶

A basic hypophosphite, $\text{BiO} \cdot \text{H}_2\text{PO}_2$, has also been described as resulting from the action of bismuthyl hydroxide, $\text{BiO} \cdot \text{OH}$, upon hypophosphorous acid.⁷ It also is unstable and appears to resemble closely the normal hypophosphite.

Bismuth Phosphite, $\text{Bi}_2(\text{HPO}_3)_3 \cdot 3\text{H}_2\text{O}$, is precipitated from a solution of ammonium phosphite by the addition of bismuth trichloride, by neutralising phosphorous acid with bismuth trioxide or hydroxide,⁸ or by the action of phosphorous acid upon an aqueous solution of bismuth nitrate and mannitol.⁹ The white needle-like crystals are only slightly soluble in water.

Bismuth Orthophosphate.—The normal salt only, BiPO_4 , is obtained by the addition of disodium phosphate to a nitric acid solution of bismuth nitrate.¹⁰ Acid salts do not appear to have been prepared.¹¹ The microscopic, monoclinic prisms of the normal salt have a density of 6.323 at 15° C. The substance is slightly soluble in bismuth trichloride, and from molecular weight determinations in this solvent the formula appears to be BiPO_4 .¹² It is reduced by heating in a current of hydrogen,¹³ but not by carbon monoxide. It is not hydrolysed by water, even after

¹ Marx, *Schweigger's J.*, 1830, 58, 471.

² Cavazzi, *Gazzetta*, 1884, 14, 219.

³ Berzelius, "*Lehrbuch*," 1826; Landgrebe, *Schweigger's J.*, 1828, 53, 460.

⁴ Hada, *J. Chem. Soc.*, 1895, 67, 229; Vanino and Hartl, *Zeitsch. anorg. Chem.*, 1906, [2], 74, 142.

⁵ Calcagno, *Semana méd.* (Buenos Aires), 1928, 35, 1042.

⁶ Vanino, *Ber.*, 1897, 30, 2001; Vanino and Treubert, *Ber.*, 1898, 31, 129.

⁷ Calcagno, *loc. cit.*

⁸ Grützner, *Arch. Pharm.*, 1897, 235, 693.

⁹ Vanino and Hartl, *J. prakt. Chem.*, 1906, [2], 74, 142. See also Calcagno, *loc. cit.*

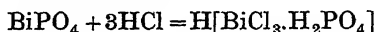
¹⁰ Chancel, *Compt. rend.*, 1860, 50, 416; 51, 882; de Schulten, *Bull. Soc. chim.*, 1903, [3], 29, 720; Calcagno, *Annales oficina quim. provincia* (Buenos Aires), 1928, 2, 1.

¹¹ Montemartini and Egidi, *Gazzetta*, 1900, 30, II, 377, 421.

¹² Caven and Hill, *J. Soc. Chem. Ind.*, 1897, 16, 29; Rügheimer, *Annalen*, 1905, 339, 349.

¹³ Heintz, *Pogg. Annalen*, 1844, 63, 567.

prolonged boiling.¹ A trihydrate, $\text{BiPO}_4 \cdot 3\text{H}_2\text{O}$, has been prepared,² and also a white, insoluble basic salt, $2\text{BiPO}_4 \cdot 3\text{Bi}_2\text{O}_3$.³ Investigation of the solubility of bismuth orthophosphate in hydrochloric acid⁴ at 25°C . indicated that it was conditioned by the concentration of the chloride ion and of the hydrogen ion, but was independent of the concentration of phosphoric acid. It is suggested that the main reaction which occurs on solution may be represented by



It has been stated that pyrophosphate and metaphosphate of bismuth cannot be prepared in the wet way owing to their rapid conversion into orthophosphate by the action of water.⁵

Bismuth Pyrophosphate, $\text{Bi}_4(\text{P}_2\text{O}_7)_3$, has, however, been prepared by the action of bismuth trioxide on molten microcosmic salt.⁶ It is a white, amorphous powder, almost insoluble in water but decomposed by it. A complex salt, *sodium bismuthi-pyrophosphate*, $\text{Na}(\text{BiP}_2\text{O}_7) \cdot 3\text{H}_2\text{O}$, has been prepared by dissolving bismuth pyrophosphate in sodium pyrophosphate. In this compound the bismuth appears to form part of the anion.⁷

Bismuth Thiophosphate is formed by the action of phosphorus pentasulphide on bismuth trichloride.⁸ It is a reddish-brown or black substance which is readily fusible without apparent decomposition and can be crystallised from the melt. It is not readily soluble in the usual solvents. It is decomposed by dilute hydrochloric acid with evolution of hydrogen sulphide; it is first oxidised and then dissolved by nitric acid. It is not attacked by solutions of alkalis.

A very unstable substance, which may be **bismuth dithiophosphate**, BiPS_2O_2 , is obtained by the action of magnesium dithiophosphate upon a bismuth salt. It is, however, readily decomposed even in ice-cold water and in alcohol.⁹

BISMUTH AND ARSENIC.

Bismuth Arsenide may be obtained by passing arsine through a solution of bismuth trichloride containing a minimum quantity of hydrochloric acid.¹⁰ It is a black substance, unattacked by water, dilute acids or alkalis, but decomposed by concentrated hydrochloric acid with formation of arsine. It is an active reducing agent.

Bismuth Arsenite.—When arsenious acid acts upon a solution of sodium bismuth chloride, a white precipitate is formed, which is stated to be bismuth arsenite, $\text{BiAsO}_3 \cdot 5\text{H}_2\text{O}$. The substance has not been obtained pure.¹¹

Bismuth Arsenate probably occurs naturally in the minerals *atelestite*, *rhagite*, *walpurkite* and *mirrite*. It may be obtained as a white crystalline substance by the action of arsenic acid or alkali arsenate upon a nitric acid solution of bismuth nitrate.¹² The *hemihydrate*,

¹ Caven and Hill, *loc. cit.* See, however, Montemartini and Egidi, *loc. cit.*

² Vanino and Hartl, *loc. cit.*

³ Cavazzi, *Gazzetta*, 1884, 14, 289.

⁴ Jensen, *Zeitsch. anorg. Chem.*, 1934, 219, 238.

⁵ Montemartini and Egidi, *loc. cit.*

⁶ Wallroth, *Bull. Soc. chim.*, 1883, [2], 39, 316.

⁷ Rosenheim and Triantaphyllides, *Ber.*, 1915, 48, 582.

⁸ Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 186.

⁹ Neogi and Ghosh, *J. Ind. Chem. Soc.*, 1929, 6, 599.

¹⁰ Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236; Berzelius, "*Lehrbuch*," 1826.

¹¹ Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

¹² de Schulten, *Bull. Soc. chim.*, 1903, [3], 29, 720; Salkowski, *J. prakt. Chem.*, 1868, 104, 170.

$\text{BiAsO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, which loses water only when heated strongly, forms microscopic monoclinic prisms, density (at 15°C.) 7.142; it is tasteless and melts only with difficulty. A **basic arsenate**, $2\text{BiAsO}_4 \cdot 3\text{Bi}_2\text{O}_3$, has also been prepared by the action of sodium arsenate upon an ammoniacal solution of bismuth citrate.¹ It forms a gelatinous precipitate, which resembles the corresponding phosphate in its chemical properties.

BISMUTH AND ANTIMONY.

No binary compound of bismuth and antimony has as yet been obtained; the two metals form a continuous series of solid solutions.²

Two **antimonates** of bismuth have been prepared by the addition of a concentrated solution of potassium meta-antimonate to a solution of bismuth ammonium citrate.³ The first, which is variously described as **bismuth oxymeta-antimonate**, $(\text{BiO})\text{SbO}_3$, or **bismuth orthoantimonate**, BiSbO_4 , is obtained as an amorphous white precipitate; while, in the presence of excess of ammonia, a **basic orthoantimonate**, $(2\text{BiO})_3\text{SbO}_4 \cdot \text{H}_2\text{O}$, is obtained as a gelatinous precipitate. The composition of the latter does not appear to have been definitely ascertained.⁴

BISMUTH AND CARBON.

Carbon will not dissolve in bismuth.⁵

Bismuth Carbonate.—The normal salt is unknown; a *basic carbonate*, $(\text{BiO})_2\text{CO}_3$, is precipitated, however, as a white powder when sodium carbonate is added to a solution of bismuth nitrate.⁶ When dried it retains from one-half to one molecule of water. The density of the product varies with the concentration and temperature of the solutions; the product of lowest density⁷ is obtained at 45°C. The basic carbonate may also be prepared from a solution of bismuth nitrate containing mannitol. An electrolytic method has also been described.⁸ The electrolyte is a 3 per cent. solution of sodium chlorate charged with excess of carbon dioxide; the anode is of bismuth and the cathode of carbon, zinc, iron or aluminium.

It has been suggested that the composition of basic bismuth carbonate is in most cases⁹ more accurately represented by the formula $\text{CO}(\text{O.BiO})_2$.

It is insoluble in water even in the presence of carbon dioxide; it is also insoluble in alkalis, but is slightly soluble in alkali carbonates. From these solutions it may be reprecipitated either by boiling, or by the addition of an alkali. It darkens in colour on exposure to light.¹⁰ It is used principally in medicinal preparations.

Basic bismuth carbonate occurs naturally in the minerals *bismutite*, *basobismutite* and *bismutosphäerite*.

Cyanides.—When potassium cyanide is added to a solution of

¹ Cavazzi, *Gazzetta*, 1884, 14, 289.

² Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 44, 131. See also pp. 42, 152.

³ Cavazzi, *Gazzetta*, 1885, 15, 37.

⁴ See also Hampe, *Zeitsch. anal. Chem.*, 1874, 13, 192.

⁵ Moissan, *Compt. rend.*, 1896, 122, 1462.

⁶ Seubert and Elton, *Zeitsch. anorg. Chem.*, 1893, 4, 44; Lefort, *Compt. rend.*, 1848, 27, 268. See also Picon, *Bull. Soc. chim.*, 1929, 45, 1056; Stickings and Coupland, *Chemist and Druggist*, 1928, 108, 605.

⁷ Jones, *Pharm. J.*, 1925, 115, 143.

⁸ Carreras, *British Patent*, 1927, 298587.

⁹ Vanino, *Pharm. Zentr.-h.*, 1911, 52, 761.

¹⁰ Tapley and Giesy, *J. Amer. Pharm. Assoc.*, 1926, 15, 46.

bismuth nitrate a brown precipitate is obtained, the composition of which is doubtful. Early investigators considered it to be an oxide, probably a peroxide, of bismuth,¹ but it was found to contain sulphur, which may have been due to impurities in the potassium cyanide.²

By triturating calculated amounts of bismuth bromide and potassium cyanide with small quantities of xylene a reaction occurs from which a complex salt, *potassium bismuthobromocyanide*, $K_3[BiBr_3(CN)_3]$, is obtained. This compound is decomposed by cold water, but is soluble in dilute hydrochloric acid, the solution however decomposing rapidly. When heated out of contact with air, potassium bromide and metallic bismuth are obtained. In a similar manner other complex salts have been obtained, such as the orange-yellow *silver salt*, $Ag_3[BiBr_3(CN)_3]$, the greenish-grey *cuprous salt*, $Cu_3[BiBr_3(CN)_3]$, and a *mercury salt*, $Hg_3[BiBr_3(CN)_3]_2$, which is at first sulphur-yellow, but changes to white prismatic needles. These salts are all decomposed by water.³

Other complex cyanides that have been obtained are *bismuth ferrocyanide*, $Bi_4[Fe(CN)_6]_3$, which is formed by precipitation with potassium ferrocyanide; ⁴ *bismuth ferricyanide*,⁵ *bismuth cobaltcyanide*, $BiCo(CN)_6 \cdot 5H_2O$, a greenish-white crystalline substance which turns blue on drying, and when dried over sulphuric acid has the formula $2BiCo(CN)_6 \cdot 7H_2O$.⁶

Bismuth Thiocyanate, $Bi(CNS)_3$, is obtained when thiocyanic acid is neutralised with bismuth hydroxide.⁷ It is possible that a basic compound is also obtained.⁸ Dilute thiocyanic acid solution must be used; basic substances are probably formed first, but on cooling, bright orange or amber-coloured rhombic crystals of normal bismuth thiocyanate separate, having the elements

$$a : b : c = 0.76134 : 1 : 0.28423$$

The crystals are decomposed by water, and on heating. The *hydrate* $Bi(CNS)_3 \cdot 14H_2O$ is obtained in the form of deep-red transparent needles by the action of excess of thiocyanic acid upon bismuth carbonate; when the acid is saturated with bismuth carbonate, **basic bismuth thiocyanate**, $Bi(CNS)_2OH \cdot 5H_2O$, separates in glistening plates on addition of alcohol.⁹

Bismuth Chromothiocyanate, $Bi[Cr(CNS)_6]$, has also been described.¹⁰

When a solution of potassium thiocyanate is added to a solution of bismuth thiocyanate, an orange-red coloration is obtained; various considerations have led to the view that solutions of bismuth thiocyanate in thiocyanic acid contain *bismuthothiocyanic acids*. It is suggested that in concentrated solutions an acid of the formula

¹ Fresenius and Haidlen, *Annalen*, 1842, 43, 135; Bödecker and Deichmann, *Annalen*, 1862, 123, 61; Muir, Hoffmeister and Robbs, *J. Chem. Soc.*, 1881, 39, 25.

² Hoffmann, *Annalen*, 1884, 223, 131.

³ Vournazos, *Compt. rend.*, 1921, 172, 535.

⁴ Werner, *Zeitsch. anal. Chem.*, 1919, 58, 23. See also Atterberg, *Bull. Soc. chim.*, 1875, [2], 24, 355; Wyruboff, *Ann. Chim. Phys.*, 1876, [5], 8, 448; Muir, *J. Chem. Soc.*, 1877, 31, 651; 1877, 32, 40.

⁵ See this Series, Vol. IX, Part II.

⁶ Fischer and Cuntze, *Chem. Zeit.*, 1902, 26, 872; Miller and Matthews, *J. Amer. Chem. Soc.*, 1900, 22, 62; Matthews, *J. Amer. Chem. Soc.*, 1900, 22, 274.

⁷ Bender, *Ber.*, 1887, 20, 723.

⁸ Meitzendorff, *Pogg. Annalen*, 1842, 56, 63.

⁹ Rosenheim and Vogelsang, *Zeitsch. anorg. Chem.*, 1906, 43, 205.

¹⁰ Tsamados and Bouzouzou, *Praktika (Akad. Athenon)*, 1929, 4, 113.

$\text{H}[\text{Bi}(\text{CNS})_4]$ is obtained, while in dilute solutions the tribasic acid, $\text{H}_3[\text{Bi}(\text{CNS})_6]$, is formed; in view of this, the formula of bismuth thiocyanate itself may be regarded as $\text{Bi}[\text{Bi}(\text{CNS})_6]$. In support of this hypothesis, a number of complex thiocyanates have been prepared, which can be represented as salts of tribasic bismuthothiocyanic acid.¹ By adding potassium thiocyanate to an aqueous solution of bismuth nitrate and mannitol, precipitating the mannitol and potassium nitrate by addition of alcohol, and crystallising from the filtrate, red, non-hygroscopic crystals of *potassium bismuthothiocyanate*, $\text{K}_3[\text{Bi}(\text{CNS})_6]$, are formed. Another potassium salt, $\text{K}_3\text{Bi}(\text{CNS})_6 \cdot 3\text{KCNS}$, has also been obtained. In a similar manner corresponding salts of *sodium* and *ammonium* have been prepared, although not in a pure condition.² By adding thallium acetate to potassium bismuthothiocyanate in appropriate proportions two complex salts of *potassium* and *thallium* have been obtained, namely, the orange-yellow salt $\text{K}_2\text{TlBi}(\text{CNS})_6$, and the pale yellow salt $\text{K}\text{Tl}_2\text{Bi}(\text{CNS})_6$. Attempts to make the pure thallium salt failed.³ Among other salts of this type that have been obtained are the *zinc salt*, $\text{Zn}_3[\text{Bi}(\text{CNS})_6]_2$, as large, non-hygroscopic, orange-red crystals; the *cobalt salt*, $\text{Co}_3[\text{Bi}(\text{CNS})_6]_2 \cdot 15\text{H}_2\text{O}$, reddish-brown crystals, the colour of this salt supporting the view that a complex bismuth anion is formed, since $\text{Bi}_2[\text{Co}(\text{CNS})_4]_3$ would presumably be dark blue; the *nickel salt*, $\text{Ni}_3[\text{Bi}(\text{CNS})_6]_2 \cdot 10\text{H}_2\text{O}$, greenish-yellow; the *vanadyl salt*, $(\text{VO})_3[\text{Bi}(\text{CNS})_6]_2 \cdot 7\text{H}_2\text{O}$, a reddish-violet powder; and the *ferric salt*, $\text{Fe}[\text{Bi}(\text{CNS})_6]$, lustrous green crystals. The *thallium salt* of monobasic bismuthothiocyanic acid, $\text{Tl}[\text{Bi}(\text{CNS})_4]$, has also been formed as red crystals.⁴

BISMUTH AND SILICON.

Bismuth Orthosilicate, $2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$, is found in nature in the minerals *eulytite* and *agricolite*, the former crystallising in the tetrahedral system and the latter in the monoclinic. Thermal and microscopical examination of mixtures of bismuth trioxide and silica revealed the existence of several silicates which have since been synthesised.⁵ These are indicated below.

Formula.	M.pt. (° C.).	Density (20° C.).
$\text{Bi}_2\text{O}_3 \cdot 8\text{SiO}_2$	992	6.628
$\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$	847	8.107
$\text{Bi}_2\text{O}_3 \cdot 2\text{SiO}_2$	873	8.657
$2\text{Bi}_2\text{O}_3 \cdot 3\text{SiO}_2$	786 to 877	8.984
$\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$	772 to 890	8.924
$3\text{Bi}_2\text{O}_3 \cdot 2\text{SiO}_2$	791	8.388
$2\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$	803 to 848	9.138
$3\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$	822	8.897
$10\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2$	832	9.136

¹ Paciello and Foà, *Gazzetta*, 1923, 53, 526.

² Vanino and Hauser, *Zeitsch. anorg. Chem.*, 1901, 28, 219.

³ Canneri and Perina, *Gazzetta*, 1922, 52, 1, 231.

⁴ Paciello and Foà, *loc. cit.* See, further, Spacu and Grecu, *Bull. Soc. stiinte Cluj*, 1932, 7, 13.

⁵ Otin, *Bull. Sci. Acad. Roumaine*, 1912-1913, 1, 189.

DETECTION AND ESTIMATION OF BISMUTH.

Detection. Dry Tests.—Bismuth compounds, when heated on a charcoal block, are reduced; a brittle globule of metallic bismuth is obtained, with a yellow incrustation of bismuth trioxide. If the original compound is mixed with powdered charcoal, potassium iodide and sulphur, and the mixture heated on a charcoal block, a scarlet incrustation is obtained.

When a mixture of metals containing bismuth is heated in a hard glass tube under a hard vacuum, a characteristic ring is formed on the tube indicating the presence of bismuth.¹ With a vacuum of 0.001 mm. the presence of 0.01 per cent. of bismuth can be detected by this method.

Wet Tests.—Bismuth is usually identified in solution by precipitation as brown trisulphide. The precipitation is effected by passing a current of hydrogen sulphide through a warm solution acidified with hydrochloric acid. The precipitate is insoluble in yellow ammonium sulphide, but is soluble in hot, dilute nitric acid and in sulphuric acid. The presence of bismuth may be confirmed by dissolving the precipitate of trisulphide in dilute nitric acid, reprecipitating the bismuth as hydroxide with ammonium hydroxide, redissolving the hydroxide in dilute hydrochloric acid, and allowing the clear solution of bismuth trichloride to drop slowly into excess of water. A copious white precipitate of bismuth oxychloride is obtained by hydrolysis.

Bismuth compounds are readily reduced by reducing agents such as formaldehyde in alkaline solution, hypophosphorous acid, or sodium or potassium stannite. In each case a black stain or residue is obtained, by means of which the presence of bismuth may be determined.

Potassium iodide reacts with solutions of bismuth salts to form black bismuth triiodide, which readily dissolves in excess of the reagent to form a yellow or orange solution which probably contains potassium iodobismuthate. This reaction may be employed as a spot test for the detection of traces of bismuth in the presence of copper, lead and cadmium.²

An electrolytic method has been suggested for the detection of bismuth in slags. A piece of the slag is connected to the positive pole of a battery and an aluminium plate to the negative pole. If a filter paper, saturated with a solution of potassium iodide, is pressed between the slag and the aluminium plate, the presence of bismuth is indicated by the formation of a reddish-yellow coloration on the filter paper.³

Bismuth may be detected in gold alloys by employing the streak test. The streak is dissolved in aqua regia, the metals are precipitated as sulphides by hydrogen sulphide, the sulphide precipitates are digested with yellow ammonium sulphide and finally dissolved in nitric acid. The presence of bismuth is detected by adding to a minute drop of this solution a drop of solution of potassium sulphate, when the double sulphate of bismuth and potassium is precipitated.⁴

Many organic reagents have been employed for the detection of bismuth. A 2 per cent. solution of 8-hydroxyquinoline containing nitric acid or sulphuric acid is mixed with a 4 per cent. solution of

¹ Tammann and Dreyer, *Zeitsch. anorg. Chem.*, 1930, 190, 53.

² Lochmann, *Zeitsch. anal. Chem.*, 1931, 85, 241.

³ Glazunov, *Chem. Listy*, 1932, 25, 352.

⁴ Strebinger and Holzer, *Mikrochemie*, 1930, 8, 264.

potassium iodide immediately before use. This reagent produces a flocculent orange precipitate when added to a solution containing bismuth if the concentration of the bismuth exceeds 1 part in 100,000. The precipitate is soluble in a mixture of acetone and ammonium acetate, and in *cyclohexane*, and these solutions may be employed in the colorimetric determination of bismuth.¹

Other reagents that have been employed are methylephredine methiodide,² viscose³ and sodium alizarinsulphonate.⁴

Estimation. Gravimetric Methods.—(1) As bismuth trioxide. Bismuth is precipitated from solution as basic bismuth carbonate, the reagent being ammonium carbonate. The precipitate is then ignited and weighed as bismuth trioxide. This method is not suitable for solutions which contain hydrochloric acid or sulphuric acid.

(2) As bismuth oxychloride. In this method the solution containing bismuth, which is faintly acid, is just neutralised by ammonium hydroxide, care being taken to avoid precipitation. The solution after neutralisation may be opalescent. A small quantity of dilute hydrochloric acid is now added, and the precipitated oxychloride allowed to settle for a considerable time. The precipitate is finally dried at 100° C. and weighed as oxychloride.

(3) As bismuth trisulphide. Hydrogen sulphide is passed through a warm, acid solution containing the bismuth, the trisulphide being precipitated. The precipitate is washed successively with a solution of hydrogen sulphide, alcohol, and freshly distilled carbon disulphide. Final washings are made with alcohol and ether, after which the precipitate is dried at 100° C. and weighed as trisulphide.

(4) As metal. (a) The method of Rose.⁵ Bismuth is precipitated as basic bismuth carbonate and the dried precipitate is reduced by fusion with potassium cyanide. The salts formed are dissolved out with water and the metal collected. (Precautions must be taken as the crucible is liable to be attacked during fusion.)

(b) The method of Vanino and Treubert.⁶ The bismuth compound in solution is reduced by the action of formaldehyde in the presence of excess of sodium hydroxide. The bismuth may either be estimated as metal, or preferably it may be redissolved in nitric acid and estimated as oxide (see method (1)). This method can be employed in the presence of hydrochloric and sulphuric acids. The results, however, are liable to be high unless special precautions are taken.

(5) Bismuth may be precipitated from its solutions by means of selenious acid.⁷ The precipitation is effected in a nitric acid solution. It is preferable to convert the bismuth selenite to bismuth trioxide before weighing.

¹ Sazerac and Pouzergues, *Compt. rend. Soc. Biol.*, 1932, 109, 79, 370.

² Feng, *J. Amer. Pharm. Assoc.*, 1932, 21, 8.

³ Tamchyna, *Chem. Listy*, 1930, 24, 31.

⁴ Germuth and Mitchell, *Amer. J. Pharm.*, 1929, 101, 46. See also Tougarinoff, *Ann. Soc. Sci. Bruxelles*, 1930, 50 B, 145; Agostini, *Ann. Chim. applicata*, 1929, 19, 164. For further literature on the detection of bismuth, see Heller, *Mikrochemie*, 1930, 8, 33; Heller and Krumholz, *ibid.*, 1929, 7, 213; Gutzeit, *Helv. Chim. Acta*, 1929, 12, 713; Tammann, Heinzel and Laars, *Zeitsch. anorg. Chem.*, 1928, 176, 143.

⁵ Rose, *Pogg. Annalen*, 1860, 110, 425.

⁶ Vanino and Treubert, *Ber.*, 1898, 31, 1303; Rupp and Hamann, *Zeitsch. anal. Chem.*, 1931, 87, 32.

⁷ Funakoshi, *J. Chem. Soc. Japan*, 1932, 53, 433; Buoherer and Meier, *Zeitsch. anal. Chem.*, 1931, 83, 352; Berg and Teitelbaum, *Zeitsch. anorg. Chem.*, 1930, 189, 101.

(6) Miscellaneous methods. Bismuth may be precipitated as a brick-red, granular complex substance, bismuth chromium thiocyanate, $\text{BiCr}(\text{CNS})_6$, by the addition of potassium chromium thiocyanate to a solution of bismuth containing nitric acid.¹ The precipitate may be dried at 120° to 130° C. and weighed. This method may be employed in the presence of iron, chromium and sulphuric acid, and it is claimed that, in certain circumstances, it is to be preferred to the selenious acid method.

Triethylenediamine cobaltic chloride has also been used as a reagent for the estimation of bismuth.² The solution of the bismuth compound is made in dilute hydrochloric acid, and is treated with potassium iodide to form potassium iodobismuthate. To this solution is added a concentrated solution of triethylenediamine cobaltic chloride, the bismuth being precipitated as a reddish-yellow, crystalline precipitate, $(\text{BiI}_4)_2(\text{Co en}_3)_2$.

"Cupferron" may be employed for the estimation of bismuth in either hydrochloric or nitric acid solution. The bismuth is ultimately determined as trioxide. This method may be employed for the separation of bismuth from many other metals.³

Volumetric Methods.—Various methods of estimating bismuth volumetrically have been described. A solution is made in nitric acid, and from this, basic bismuth oxalate is precipitated with ammonium oxalate. This precipitate is then dissolved in hydrochloric acid, the solution neutralised with ammonium hydroxide, and any precipitated hydroxide redissolved in sulphuric acid. This final solution is then heated to 70° C. and titrated with a standard solution of potassium permanganate.

The following indirect method may also be noted. To a fairly acid solution containing bismuth, a solution of potassium bromide is added until the precipitate of bismuth oxybromide which forms at first is redissolved. The solution is now neutralised with sodium hydroxide and a freshly prepared, saturated solution of $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ is added in excess. The precipitate is then distilled with a solution of sodium hydroxide and the expelled ammonia collected in a known volume of standard acid solution, the excess of which is ultimately titrated with a standard solution of sodium hydroxide. In this reaction six molecules of ammonia are equivalent to one atom of bismuth.⁴

Other volumetric methods are mentioned in the section on the microchemical estimation of bismuth.

Colorimetric Methods.—The yellow-orange or red colour produced by the solution of bismuth triiodide in excess of potassium iodide is frequently employed for the colorimetric estimation of bismuth. The sample is dissolved in nitric acid, glycerine is added, followed by a solution of potassium iodide. Comparison is made by a similarly treated standard solution containing bismuth.⁵

¹ Mahr, *Zeitsch. anorg. Chem.*, 1932, 208, 313.

² Spacu and Suci, *Zeitsch. anal. Chem.*, 1929, 79, 196.

³ Pinkus and Dernies, *Bull. Soc. chim. Belg.*, 1928, 37, 267. For further literature on the gravimetric estimation of bismuth, see Ishimaru, *J. Chem. Soc. Japan*, 1932, 53, 566; Lee, *ibid.*, 1931, 52, 229; Calloway, Jun., *J. Assoc. Official Agr. Chem.*, 1931, 14, 347; Solodovnikov, *Sci. Rep. State Univ. Kajan*, 1928, 88, 457.

⁴ Mahr, *Zeitsch. anal. Chem.*, 1933, 93, 433.

⁵ Thresh, *Pharm. J.*, 1880, [3], 10, 641. See also Valyashko and Virup, *Ukrainskii Khem. Zhur.*, 1930, 5, 275, 293; Frick and Engemann, *Chem. Zeit.*, 1929, 53, 505; Portnov and Skvorzov, *Farm. Zhur.*, 1928, 534; *Chem. Zentr.*, 1929, 1, 114.

Thiourea may also be employed in the colorimetric estimation of bismuth. Solid thiourea is added to a bismuth solution containing a slight excess of acid. A yellow coloration is obtained, due to the formation of various complex compounds, and may be compared with the colour obtained with a standard solution containing bismuth. If ferric iron is present, the solution should be boiled with hydrazine sulphate.¹

If a solution of bismuth nitrate is added to a solution of cinchonine potassium iodide a crimson or orange coloration is produced, the intensity of the colour depending upon the amount of bismuth present. Lead, arsenic, antimony and tin must first be removed, and the bismuth solution must be added to the reagent. Comparison is made with the colour obtained with a standard bismuth solution. This method is suitable for the estimation of small amounts of bismuth of the order of 0.00008 to 0.00015 gram.²

Microchemical Methods.—A volumetric method has been devised for the micro-estimation of bismuth. The bismuth is precipitated as oxyiodide and the precipitate is decomposed by treatment with a solution of potassium hydroxide. The iodide present is then oxidised to iodate by the action of chlorine, potassium iodide is added and the liberated iodine titrated with a standard solution of sodium thiosulphate.³

A concentrated solution of *trans*-dithiocyanato-diethylenediaminocobaltic thiocyanate reacts with a faintly acid solution of bismuth nitrate (to which excess of potassium iodide has been added) to form the orange-yellow compound dithiocyanato-diethylenediaminocobaltic iodobismuthate, $[\text{Co en}_2(\text{SCN})_2]\text{BiI}_4$. This reaction may be employed both for macro- and micro-estimation of bismuth.⁴

Other reagents which have been suggested for use in the micro-estimation of bismuth are quinoline,⁵ a solution of piperazine in acetone,⁶ viscose,⁷ and hexamethylene-tetramine.⁸

Electrolytic Methods.—Bismuth may be estimated electrolytically in acid solution. A nitric acid solution is frequently employed containing not more than 2 per cent. of free acid.⁹ Hydrazine hydrate may be employed as a reducing agent, the electrolysis being carried out at 80° to 85° C. using a 0.01N HNO_3 , | quinone auxiliary electrode, a current of 1.3 amperes, and a cathode potential (referred to the quinone electrode) of -0.45 to -0.6 volt. This method is suitable for the separation of bismuth from lead.¹⁰ A solution of bismuth trichloride may also be used; it is suggested that the solution should also contain sodium chloride, calcium chloride or magnesium chloride. Additions of pyrogallol and resorcinol to the electrolyte improve the deposit, but additions of hydroquinone and benzoic acid are not so effective.¹¹

¹ Mahr, *Zeitsch. anal. Chem.*, 1933, 94, 161.

² For further reference to colorimetric methods of estimating bismuth, see Sazerac and Pouzergues, *loc. cit.*; Teitelbaum, *Zeitsch. anal. Chem.*, 1930, 82, 366.

³ Straub, *Zeitsch. anal. Chem.*, 1929, 76, 108.

⁴ Spacu and Spacu, *ibid.*, 1933, 93, 260.

⁵ Korenman, *Pharm. Zentr.-h.*, 1930, 71, 769.

⁶ Martini, *Mikrochemie*, 1928, 6, 28; *Chem. Zentr.*, 1928, i, 1894.

⁷ Tamchyna, *loc. cit.*

⁸ Korenman, *Pharm. Zentr.-h.*, 1929, 70, 1. See also Rosenthaler, *Pharm. Zeit.*, 1929, 74, 1272; Dumont and Bouillenne, *Compt. rend. Soc. Biol.*, 1928, 99, 1247.

⁹ Lucchi and Bartocci, *Ann. Chim. applicata*, 1932, 22, 509.

¹⁰ Collin, *Analyst*, 1929, 54, 654.

¹¹ Kern and Jones, *Trans. Amer. Electrochem. Soc.*, 1930, 57, 255.

Good deposits of bismuth are obtained from an electrolyte of perchloric acid containing bismuth, with a little oil of cloves as an addition agent. The electrolysis is carried out at 40° C. with a current density of 1.2 to 3.6 amperes per square foot. If lead is present, however, both lead and bismuth are deposited.¹

The dropping mercury electrode may also be employed for the electrolytic estimation of bismuth. The electrolyte is composed of a nitric acid solution, neutralised by sodium hydroxide, to which Rochelle salt has been added.²

Spectrographic Methods.—In recent years spectrographic methods have been adopted for the identification and the approximate estimation of bismuth. These methods have been employed mainly in connection with alloys, but they have also been adopted in the examination of ash from organic remains.³

¹ Fink and Gray, *Trans. Amer. Electrochem. Soc.*, 1932, 62, 189.

² Suchy, *Collection Czechoslov. Chem. Comm.*, 1931, 3, 354. For further references to the electrolytic estimation of bismuth, see Chetverikov, *Tzvet. Met.*, 1930, 5, 645; Grosset, *Bull. Soc. chim. Belg.*, 1933, 42, 269; Jilek and Lukas, *Collection Czechoslov. Chem. Comm.*, 1929, 1, 369.

³ Eddy, *Chem. Eng. Mining Review*, 1932, 24, 239; Brownsden and van Someren, *J. Inst. Metals*, 1931, 46, 97; Lomakin, *Zeitsch. anorg. Chem.*, 1930, 187, 75; Eddy and Laby, *Proc. Roy. Soc.*, 1930, A 127, 20; Piccardi, *Atti R. Accad. Lincei*, 1929, 10, 258.

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